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EMISSION SPECTRA FROM SOLIDS CONDENSED AT VERY LOW TEMPERATURES FROM THE ELECTRICAL DISCHARGE PRODUCTS OF NITROGEN-CARBON MONOXIDE AND NITROGEN-ACETYLENE MIXTURES

By S. L. N. G. Krishnamachari,* R. W. Nicholls‡ and H. P. Broida

(*National Bureau of Standards, Washington, D.C.*)

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Introduction

In a previous report[1] on the spectrum of the condensed deposits (4·2° K.) of microwave discharge products of nitrogen and carbon monoxide mixtures, a set of closely spaced diffuse bands between 3000 and 4600 Å were described. The present paper describes a second set of widely spaced, relatively sharper bands obtained from these solids under slightly different conditions. These bands are designated as sharp bands to distinguish them from the above-mentioned diffuse bands, though in reality they are not very sharp. Both sharp and diffuse bands have been obtained as well from the condensed deposits of discharge products of nitrogen and acetylene mixtures. The spectra also have been obtained by isotopic substitution with the following molecules, N_2^{15}, $C^{12}O^{18}$, $C^{13}O^{16}$ and C_2D_2. A shift of the bands (both sharp and diffuse) was found only for C^{13} and not for the other isotopes.

Experimental

The experimental arrangement, consisting of a microwave oscillator, a low temperature Dewar and a gas flow system, was similar to that described previously.[1] Spectra were recorded on two grating spectrographs (an *f*/0·6 spectrograph with glass optics and a dispersion of 330 Å/mm. and an *f*/2·0 spectrograph with quartz optics and a dispersion of 20 Å/mm.) and an *f*/4 quartz prism spectrograph. Kodak 103 *a*–O and 103 *a*–F films and plates were used and times of exposure varied from 5 seconds to

* This author was temporarily on leave from Atomic Energy Establishment, Trombay, Bombay, India.

‡ Temporarily on leave from the University of Western Ontario, London, Ontario.

4 minutes; longer exposures (8 or 10 minutes) did not bring out any additional bands.

The sharp bands were best obtained in this system with a nitrogen flow of 15 cm.^{3}/min. (NTP) and a carbon monoxide or acetylene flow of 1 cm.^{3}/min. (NTP). Even though higher carbon monoxide flow rates (up to 60% CO in the total mixture) bring out these bands, no definite advantage was found in using flow rates higher than 1 cm.^{3}/min., which was the lowest value that could be reproducibly measured with the flow meters that were used. Pre-purified nitrogen (purity 99·996%) and CP grade carbon monoxide (99·5% purity) were used for these experiments.

Two methods were used successfully with nitrogen and acetylene. In one method, the acetylene was mixed with nitrogen before entering the discharge region, as in the CO case. In the other method the acetylene was added to the discharge products of nitrogen about 5 cm. away from the cold finger. In the latter case the usual atomic flame was observed in the gas phase and the method essentially consisted in "freezing the atomic flame". The two methods gave the same spectra.

Experiments with carbon dioxide and nitrogen did not show the sharp or the diffuse bands. In the case of the discharge products of carbon dioxide condensed in an argon matrix, the spectra have shown the A bands (Herzberg bands)[2] of O_2 and a group of four bands at 5320, 5715, 6190 and 6743 Å. These latter bands may be Atmospheric Bands of O_2.

In both the carbon monoxide and the acetylene experiments the luminescence from the condensed deposit was violet in colour. As soon as the carbon monoxide (or acetylene) flow was stopped, allowing the nitrogen flow to continue, the luminescence changed from violet to bluish-green. The spectrum of this solid glow showed the diffuse bands previously described.[1] The bluish-green glow could be continued for more than an hour, the length of time depending on the amount of carbon monoxide or acetylene initially deposited. It should be pointed out that during the deposition of the nitrogen and carbon monoxide (or acetylene) mixtures, there also was emission from the gas near the solid. A weak pink glow could be observed surrounding the bottom tip of the cold finger. The spectrum of this gas-phase glow showed the violet and red systems of CN.

Isotopic nitrogen 15 at 50% and 90% concentration was used. For the higher concentration case, the evaporated sample containing nitrogen and carbon monoxide was mass-spectrometrically analysed and gave a ratio

2·5:1·3:1 for the mass numbers 28, 29 and 30. The O^{18} and C^{13}* (used in the form of CO) each had an isotopic concentration of 65% which was determined mass-spectrometrically before using it in the experiments. The deuterated acetylene used had a nominal deuterium concentration of 98%.

Most of the present series of experiments were conducted at liquid hydrogen temperatures because of its lower evaporation rate and because no difference in wavelengths, relative intensities or breadth of the sharp or the diffuse bands was observed at liquid helium temperatures. The only difference in the spectra was that at liquid helium temperatures the α-line of nitrogen was much stronger than the β-line of oxygen, while at liquid hydrogen temperatures the reverse was the case. This temperature effect agrees with the earlier observations on α and β[3].

Results

The spectrum of the violet glow which gave the sharp bands is shown in Fig. 1. The upper spectrum was obtained during condensation and the lower spectrum was obtained during the warming of the condensed solid, after the refrigerant in the Dewar had evaporated. These spectra show a group of six strong bands with weaker components approximately midway between them.

In Tables I *a* and I *b* estimated eye intensities, wavelengths of the center of bands, widths of the bands, wavenumbers and wavenumber intervals of the sharp bands are given. These measurements are average values taken from a number of spectra on all three spectrographs. Table I *a* presents the data for the stronger bands while Table I *b* gives the data for the weaker components. The wavenumber interval is roughly the same for the stronger and weaker bands and is 2280 cm.$^{-1}$ (with a maximum deviation of 80 cm.$^{-1}$). This frequency probably represents a common ground-state frequency for bands arising from two different vibrational levels of the upper electronic state. The strong bands, because of their high intensity, might arise from the zero vibrational level while the weaker ones might arise from a single quantum excitation of a vibrational frequency of about 1320 cm.$^{-1}$ (maximum deviation of 30 cm.$^{-1}$) in the upper electronic state.

Figure 2 shows the diffuse bands obtained when the flow of carbon monoxide (or acetylene) was stopped and the glow changed from violet to bluish-green. The band data are given in Table II. The wavenumber interval between these bands is of the order of 670 cm.$^{-1}$ (maximum deviation

* We are grateful to Dr. Robert Ferguson for preparing and supplying us $C^{13}O$.

TABLE I

Sharp bands

Intensity	(Centre) A	Breadth A	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
(*a*) Stronger bands:				
4	3013	10	33180	
				2306
8	3238	10	30874	
				2327
10	3502	10	28547	
				2266
9	3804	10	26281	
				2278
5	4165	10	24003	
				2242
2	4594	10	21761	
(*b*) Weaker components:				
1	3108	5	32166	
				2297
2	3347	5	29869	
				2245
2	3619	5	27624	
				2315
1	3950	5	25309	
				2205
1	4327	5	23104	
				2320
0	4810	5	20784	

100 cm.$^{-1}$). The data on the diffuse bands is in agreement with that previously reported.[1]

Of the isotopes studied, only C^{13} produced definite and measurable shifts. Shifts occur for both the sharp and the diffuse bands. Figure 3 shows a comparison of the spectrum of the sharp and diffuse bands obtained with C^{13} and with C^{12}. The band data for C^{13} are given in Table III with a comparison of C^{12} obtained with the same spectrograph. There is no shift for the first member of the sharp bands, *i.e.*, the 3010 Å band, and thus this band probably is the origin of the system. The other members of this series show a gradual increase in the width of the band, and a gradual shift

TABLE II

Diffuse bands

Intensity	(Centre) A	Breadth A	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$	Blend with sharp band
1	2895	20	34523		..
				644	
2	2950	20	33888		..
				675	
6	3010	20	33213		×
				628	
3	3068	25	32585		..
				767	
4	3142	25	31818		..
				694	
5	3212	25	31124		×
				673	
4	3283	25	30451		..
				707	
5	3361	25	29744		×
				649	
6	3436	25	29095		..
				678	
6	3518	25	28417		×
				739	
8	3612	25	27678		×
				651	
8	3699	25	27027		..
				705	
8	3798	25	26322		×
				642	
10	3893	25	25680		..
				643	
9	3993	25	25037		..
				654	
9	4100	25	24383		..
				654	
8	4213	25	23729		..
				566	
6	4316	25	23163		..
				667	
5	4444	25	22496		..
				711	
6	4589	25	21785		×
				689	
1	4739	25	21096		..
				664	
0	4893	25	20432		..

TABLE III

Carbon^{13} *substitution*

Intensity	Designation	(Centre) A	Breadth A	$\nu(C^{13})$ cm.$^{-1}$	$\nu(C^{12})$ cm.$^{-1}$	(C^{13-12}) cm.$^{-1}$
5	Sharp	3010	10	33213	33213	0
1	Diffuse	3140	15	31838	31808	30
3	Diffuse	3204	15	31202	31115	87
10	Sharp	3232	18	30932	30889	48
2	Diffuse	3278	20	30498	30423	75
3	Diffuse	3349	25	29851	29745	106
2	Diffuse	3432	25	29129	29053	76
10	Sharp	3489	22	28653	28571	82
3	Diffuse	3599	30	27778	27708	70
2	Diffuse	3687	30	27115	27027	88
6	Sharp	3782	20	26434	26288	146
1	Diffuse	3876	25	25793	25680	113
1	Diffuse	3978	..	25131	25024	107
1	Sharp	4117	10	24283	24037	246
1	Sharp	4143	8	24130	24037	93

in the center of gravity of the band toward shorter wavelengths. The fifth member, *i.e.*, the band at 4170 Å (this was too weak to be reproduced in Fig. 3) shows two relatively broad components separated by 150 cm.$^{-1}$ The one at the shorter wavelength is nearly twice as strong as the one at the longer wavelength. The components are shifted toward shorter wavelengths by 93 and 246 cm.$^{-1}$ with respect to the C^{12} spectrum. If there are two carbon atoms in the emitter, one would expect, for the C^{13} concentration is 65%, three components corresponding to C_2^{12}, $C^{12}C^{13}$ and C_2^{13}. The component corresponding to C_2^{12} should be unshifted. Surprisingly enough, in the present case no unshifted component was observed. The diffuse bands

show a broadening and a shift toward shorter wavelengths with the C^{13} substitution.

The present experiments with the isotopes do not indicate the presence of nitrogen, oxygen or hydrogen atoms in the emitter, since no shifts were observed with the appropriate isotopes. Thus the previous[1] assignment of the diffuse bands to NCO and the sharp bands to CO_2^+ is not confirmed. There is a definite effect of the C^{13} isotope and an indication that at least two carbon atoms might be present in the emitters. The fact that the vibrational frequency (2280 cm.$^{-1}$) of the sharp bands is much higher than the ground-state frequency (1640 cm.$^{-1}$) of C_2 molecule suggests that the emitter may not be a simple diatomic molecule, but that it might contain more atoms which increase the carbon-carbon stretching frequency. Unfortunately, additional experiments have not given more information and the data are not sufficient to permit a reasonable assignment to the emitters nor to understand the mechanisms by which the two sets of bands are formed.

One of us (S. L. N. G. Krishnamachari) acknowledges the award of an I.C.A. Fellowship during the tenure of which this work was performed.

Summary

Two unidentified series of emission bands (sharp and diffuse) between 2900 and 4900 Å were observed at 4·2° and 20·4° K. These bands were emitted from the condensed products of microwave discharges in nitrogen-carbon monoxide and nitrogen-acetylene mixtures. The sharp 'series are characterised by a frequency difference of 2280 cm.$^{-1}$ and the diffuse series by a frequency difference of 670 cm.$^{-1}$ Isotopic substitution shows at least one carbon atom is present in the emitting species.

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Explanation of Plate I

Fig. 1. Sharp bands. Liquid helium temperature; *f*/4 quartz spectrograph; 103*a*-F emulsion; slit width 350 μ; CO and N_2 each at a flow rate of 7·5 cm.^{3}/min. Exposure time for the glow is 10 minutes and for the warm-up is 3 minutes. Hg arc comparison spectrum taken with 20 μ slit.

FIG. 2. Diffuse bands. Liquid hydrogen temperature; *f*/4 quartz spectrograph; 103*a*-F emulsion; slit width 100 μ; N_2 flow 7·5 cm.^{3}/min. for 2 minutes. Exposures are from the same negative, the top and bottom parts are exposed for 3 and 6 minutes respectively. Hg arc comparison spectrum taken with 20 μ slit.

FIG. 3. C^{13} isotope effect. Liquid hydrogen temperature; *f*/2 grating spectrograph; 103*a*-O emulsion; spectrum at the top obtained with nitrogen flow of 15 cm.^{3}/min. and carbon monoxide flow of 1 cm.^{3}/min.; C^{13} isotopic concentration 65%; exposure time 40 seconds; spectrum at the bottom obtained with nitrogen flow 15 cm.^{3}/min. and carbon monoxide flow 1 cm.^{3}/min.; exposure time 60 seconds; slit width 400 μ; Hg arc comparison taken with the same slit width.

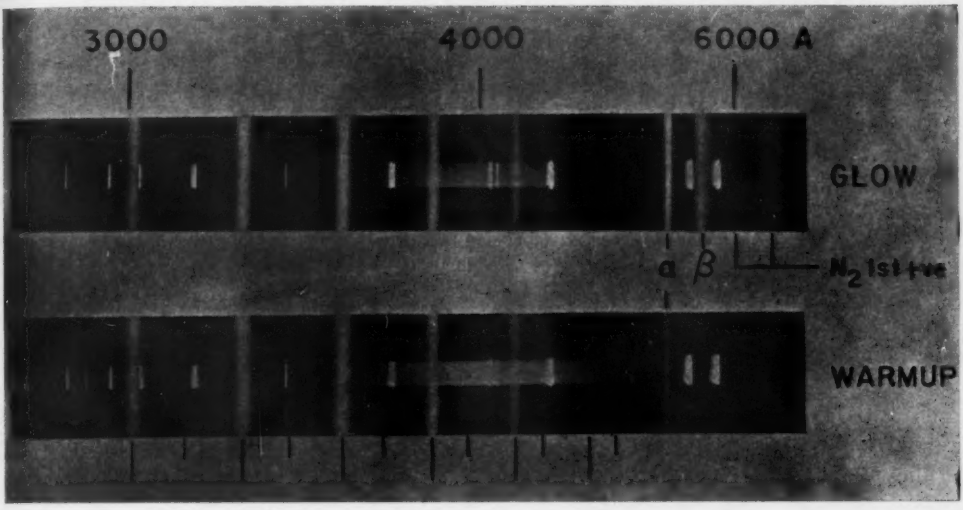

FIG. 1

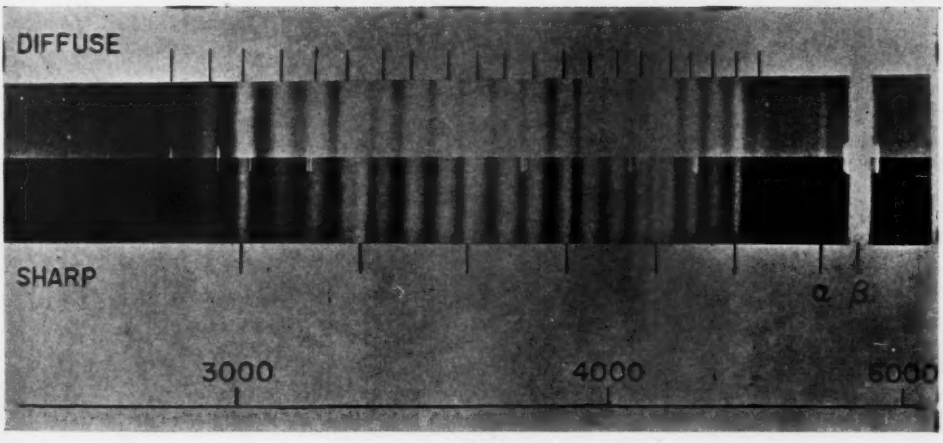

FIG. 2

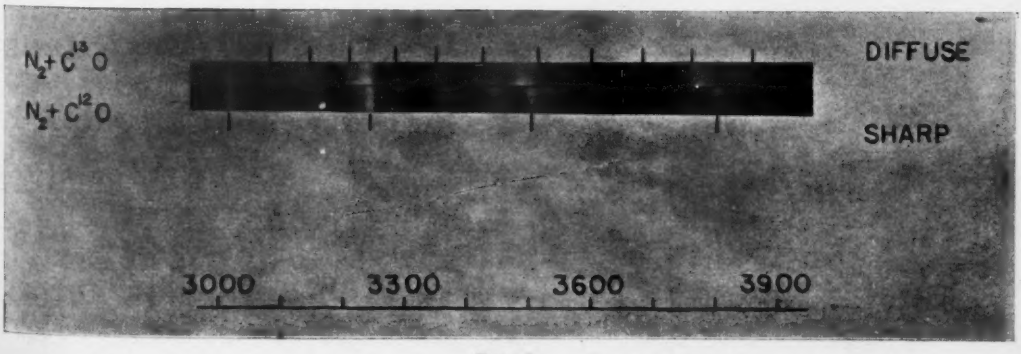

FIG. 3

THE INFRA-RED AND RAMAN SPECTROSCOPIC STUDIES OF AMIDES

By P. G. Puranik and K. Venkata Ramiah

(*Department of Physics, University College of Science, Osmania University, Hyderabad-7*)

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I. Introduction

The infra-red absorption spectroscopic studies of primary and secondary amides have been mainly devoted to the investigations of the possible existence of keto, enolic forms in these compounds. Lecomte *et al.*[1] and Evans[2] have recorded the infra-red spectrum of formamide and the authors[3] have investigated the association of this amide. Randall *et al.*[4] recorded the spectra of pure amides and Urazouskii *et al.*,[5] Mansel Davies and Hallam[6] have studied the infra-red spectrum of acetamide. Richard and Thompson[7] have investigated the $3\,\mu$ and $6\,\mu$ regions of a number of amides. From the data of the shifts in the frequencies of some of the absorption bands in the $6\,\mu$ region, they have concluded that these compounds have keto structure. Similar conclusions were drawn by the Oxford workers[8] who studied secondary amides having structures analogous to penicillin. Thus in the case of all amides other than formamide, the earlier workers confined their attention to the elucidation of keto structure for amides. The assignments of the N—H stretching frequencies of the primary amides by the earlier workers is only qualitative and empirical. Norman Jones *et al.*[9] have drawn attention to the fact that the assignments of the bands in the $3\,\mu$ region of N--H stretching vibrations of primary amides is still uncertain.

The authors have investigated the associations in some of the amides with a view to study

(*a*) the spectroscopic evidence for the dimeric manifestation of primary and secondary amides under investigation,

(*b*) the assignments of the N—H stretching frequencies on quantitative basis,

(*c*) the effect of various donor solvents on the frequencies of the functional groups, such as the N—H stretching, deformation and the carbonyl stretching absorption bands,

(*d*) the shifts in the C=O stretching frequencies of the amides in solution of dioxane in the presence of phenol and

(*e*) the shifts in the Raman frequencies of N-methyl formamide and dimethyl formamide in various solvents.

II. EXPERIMENTAL

A Perkin-Elmer Infra-red Spectrophotometer Model 21 with NaCl optics was used to obtain the spectra. The infra-red spectra of solids were obtained by the mull technique. A pair of matched cells of thickness 0·94 mm. was used for studying the apparent molecular extinction coefficients of the absorption bands in the 3 μ region in solutions. To study the solvent effect on the functional groups, matched cells of 0·1 mm. thickness were used. A spectral slit-width of 10 cm.$^{-1}$ was used to record the N—H stretching absorption bands. The molar concentrations are expressed to two significant figures for values more than 0·1 molar and to three significant figures for lower concentrations. The apparent molecular extinction coefficients 'ϵ_{max}' have been calculated to two significant figures.

The experimental technique to obtain Raman spectra of pure substances and compare the shifts in some of the lines in mixtures has been the same as described by the authors.[3]

III. RESULTS

The N—H stretching frequencies of pure amides and in various solvents are given in Table I. The N—H stretching frequencies of formamide and in solutions of chloroform and dioxane[3] are given for comparison. The infra-red spectra of solid acetamide, benzamide and butyramide have two absorption bands in the region of 3350 and 3200 cm.$^{-1}$ and in solutions of chloroform two additional bands appear in the region of 3530 and 3430 cm.$^{-1}$ With the increasing dilution of the amides in chloroform, the bands in the region of 3530 and 3430 cm.$^{-1}$ become more prominent and the intensity of the other two bands in the region of 3350 and 3200 cm.$^{-1}$ decreases. Davies and Hallam[6] report a band at 3501 wave numbers in acetamide and they assign this band to the N—H asymmetric stretching of the associated molecules. The infra-red spectrum of acetamide (nujol mull) or of it in solution of chloroform, as recorded by the authors, did not give any indication of the presence of a band at 3501 cm.$^{-1}$ A band in similar position could not be recorded even in case of benzamide and butyramide.

TABLE I

N—H stretching, N—H deformation and C=O stretching absorption bands of amides in various solvents (cm.$^{-1}$)

Amide	Nature of vibration	Pure amide	In chloroform	In dioxane	In acetonitrile	In pyridine
	N–H stretch	3378, 3280, 3200	3536, 3439, 3364, 3280, 3210	3443, 3357, 3211 (w)	3480, 3365 3215 (w)	3310, 3185
Formamide ..	N—H Deform	1618	1592	1609	1603	1617
	C=O stretch	1716, 1698	1716	1718	1715	1718
	N—H Stretch	3355, 3205	3520, 3430, 3360, 3205	3450, 3360, 3220 (w)	3470, 3380, 3220 (w)	3310, 3185
Acetamide ..	N—H Deform	1631	1595	1615	1613	1621
	C=O Stretch	1661	1684	1689	1684	1684
..	N—H Stretch	3370, 3175	3535, 3430, 3370, 3200	3450, 3360, 3210 (w)	3480, 3380, 3225 (w)	3335, 3215
Benzamide ..	N—H Deform	1626	1603	1613	1610	1618
..	C=O Stretch	1664	1681	1686	1685	1681
..	N—H Stretch	3325, 3180	3530, 3415, 3345, 3185	3450, 3360, 3210 (w)	3480, 3380, 3210 (w)	3335, 3190,
Butyramide ..	N—H Deform	1631	1592	1613	1610	1621
..	C=O Stretch	1661	1681	1690	1684	1684
..	N—H Stretch	3300	3470, 3345	3370	3385	3270
N-methyl formamide	Amide II	1546	1546, 1486 (w)	1546, 1534 (w)	1546, 1531 (w)	1546, 1534 (w)
..	C=O Stretch	1667, 1695	1695	1695	1695	1695

The Raman spectrum of N-methyl formamide is in agreement with the one recorded by Tatsuo Miyazawa *et al.*[10] The Raman frequencies of dimethyl formamide are:

239 (2), 316 (3), 354 (4), 405 (5), 604 (0), 666 (7), 769 (0), 866 (6), 987 (5), 1094 (4 *b*), 1407 (6), 1442 (6), 1664 (4), 2873 (5), 2945 (5) and 3006 (2) cm.$^{-1}$

The infra-red spectrum of N-methyl formamide as recorded by the authors is in agreement with that reported by DeGraaf and Sutherland.[11]

IV. DISCUSSION

N—H Stretching absorption bands.—The functional groups responsible for the associations in the primary and secondary amides are the amino and the carbonyl groups forming intermolecular associations of the N—H...O=C type. The absorption spectra of these substances in solutions, therefore, contain characteristic bands of N—H and C=O vibrations of the monomer and the associated molecules. The apparent molecular extinction coefficients (ϵ_{max}) of the absorption bands in the region of 3520, 3430, 3360 and 3200 cm.$^{-1}$ have been calculated at various concentrations in solutions of chloroform in case of acetamide, benzamide and butyramide. These observations are given in Table II.

If monomers and dimers are in dynamic equilibrium in solution at a molar concentration 'c', then from the considerations of Law of Mass Action, the ratio $c\epsilon^2_{max}(\text{m.})/\epsilon_{max}(d)$ is a constant; $\epsilon_{max}(m)$ is the apparent molecular extinction coefficient of the band of a functional group such as the N—H stretching vibration of the monomer and $\epsilon_{max}(d)$ that of the band due to the same mode of vibration of the dimer. Hence the constancy of $c\epsilon^2_{max}(m)/\epsilon_{max}(d)$ in case of any two absorption bands is a consequence of the fact that these bands arise out of the same modes of vibrations of the monomer and dimer molecules. The authors[3,12] have used similar expressions in their studies of the associations of formamide and amino-pyridines.

The values of $c\epsilon^2_{max}(a)/\epsilon_{max}(d_1)$ have been calculated at different concentrations for pairs of bands at 3520 and 3360; 3535 and 3370; 3530 and 3345 cm.$^{-1}$ in case of acetamide, benzamide and butyramide respectively and these results are given in Table II. In case of each pair of bands, $\epsilon_{max}(a)$ is the apparent molecular extinction coefficient of the band at higher frequency and $\epsilon_{max}(d_1)$ that of the band at lower frequency. These ratios are constant to about 6 per cent. indicating that in case of each pair of bands, if the band at higher frequency is due to N—H asymmetric stretch of the monomers, then the one at lower frequency is due to the N—H asymmetric

TABLE II

Apparent molecular extinction coefficients of N—H stretching absorption bands of primary amides in solutions of chloroform

Amide	Mol. conc.	Free N—H bands		Bonded N—H bands		$c\epsilon^2_{max}(a)$ / $\epsilon_{max}(d_1)$	$c\epsilon^2_{max}(s)$ / $\epsilon_{max}(d_2)$
		$\epsilon_{max}(a)$	$\epsilon_{max}(s)$	$\epsilon_{max}(d_1)$	$\epsilon_{max}(d_2)$		
Acetamide	.. 0·19	24	27	19	18	5·8	7·7
	.. 0·16	25	28	17	16	5·9	7·8
	.. 0·093	32	35	16	15	6·0	7·6
	.. 0·062	36	39	14	12	5·7	7·9
Benzamide	.. 0·16	26	29	21	22	5·2	6·1
	.. 0·12	28	32	19	20	5·0	6·1
	.. 0·083	30	37	16	17	4·7	6·7
	.. 0·05	36	45	14	15	4·6	6·8
Butyramide	.. 0·27	23	24	20	20	7·1	7·8
	.. 0·16	29	30	19	19	7·1	7·6
	.. 0·10	34	36	16	15	7·2	8·6
	.. 0·069	37	40	15	13	6·3	8·5

stretch of the dimers. Similarly, the values of $c\epsilon^2_{max}(s)/\epsilon_{max}(d_2)$ have been calculated at different concentrations for the pairs of bands at 3430 and 3205 in acetamide, 3430 and 3200 in benzamide and 3413 and 3185 cm.$^{-1}$ in butyramide and these observations are also given in Table II. The ratios in this case are constant to about 6 per cent. As in the case of asymmetric stretch, if the band at higher frequency is due to N—H symmetric stretch of the monomers, then the one at lower frequency is due to the same mode of vibrations of dimers. Thus in the region of 3520, 3530, 3370 and 3200 cm.$^{-1}$, the first two absorption bands are assigned to N—H asymmetric and symmetric stretching vibrations of the monomers and the other two to the same modes of vibrations of the dimers.

The infra-red absorption band due to N—H stretch of N-methyl formamide is at 3300 cm.$^{-1}$ which happens to be broad and strong. The corresponding Raman frequency has a banded structure extending from 3278 to 3358 cm.$^{-1}$ with a visual intensity 3. But in solutions of carbon tetrachloride or chloroform an additional band appears at 3470 cm^{-1} in the infra-red spectrum and the band at 3300 cm.$^{-1}$ shifts to 3345 cm.$^{-1}$ The value of the ratio $c\epsilon^2_{max}(m)/\epsilon_{max}(d)$ has been calculated at different concentrations for the two absorption bands at 3470 and 3345 cm.$^{-1}$ in carbon tetrachloride and chloroform and these observations are given in Table III.

TABLE III

Apparent molecular extinction coefficients of N—H stretching absorption bands of N-methyl formamide in carbon tetrachloride and chloroform

Solvent	Mol. conc.	Free N—H band $\epsilon_{max}(m)$	Bonded N—H band $\epsilon_{max}(d)$	$\frac{c\epsilon^2_{max}(m)}{\epsilon_{max}(d)}$
CCl_4 ..	0·15	17	31	1·39
..	0·10	19	29	1·25
..	0·065	25	28	1·45
$CHCl_3$ ..	0·22	24	18	7·04
..	0·19	25	16	7·42
..	0·13	29	14	7·80
..	0·085	34	13	7·56

It is seen from Table III that the ratios are constant to about 8 per cent. indicating that if the band at 3470 cm.$^{-1}$ is due to N—H stretching vibrations of the monomers, the one at 3345 cm.$^{-1}$ is due to the same mode of the vibrations of the dimer.

The apparent molecular extinction coefficients of the absorption bands of the amides in the C—H stretching region are obtained in solutions of chloroform at the same concentrations at which ϵ_{max} of the N—H stretching absorption bands are calculated. They are found to be constant at these concentrations and the values are 15, 14, 23 and 25 in the cases of acetamide, benz-

amide, butyramide and N-methyl formamide for frequencies at 2965, 2965, 2880, and 2880 cm.$^{-1}$ respectively.

The carbonyl and N—H deformation bands.—The frequencies of C=O and N—H in-plane deformation bands of the amides and in solutions of chloroform are given in Table I. The C=O stretching band of the solid acetamide is at 1661 cm.$^{-1}$ but in strong solutions of chloroform, three distinct peaks could be recorded at 1712, 1684 and 1666 cm.$^{-1}$; the peak at the lowest frequency being the strongest of the bands. With the increasing dilution of the amide the peak at 1666 cm.$^{-1}$ disappeared completely, but the bands at 1712 and 1684 cm.$^{-1}$ could be recorded at a molar concentration of 0·008. Even at this low concentration where the molecules dissociate considerably, the band at 1684 cm.$^{-1}$ is very strong and the one at 1712 cm.$^{-1}$ is much weaker. The corresponding frequencies in dilute solutions of dioxane are at 1712 and 1689 cm.$^{-1}$ Therefore, the authors propose to assign the band at 1684 cm.$^{-1}$ in chloroform or at 1689 cm.$^{-1}$ in dioxane as one due to the C=O stretching vibrations of the monomers and the one at 1661 cm.$^{-1}$ in the solid or at 1666 cm.$^{-1}$ in chloroform as of the associated molecules. The frequency of the C=O stretch of the other amides increases in solutions of chloroform and donor solvents to the extent of 25 cm.$^{-1}$ as can be seen from Table I.

The N—H in-plane deformation bands shift to lower frequencies to the extent of 25 to 30 cm.$^{-1}$ and become sharp in solutions of chloroform. The N—H in-plane deformation band of solid acetamide, which is at 1631 cm.$^{-1}$, shifts to 1595 cm.$^{-1}$ in dilute solutions of chloroform and similar results are obtained in case of other primary amides. Thus the authors assign the band at higher frequency to N—H in-plane deformation of the associated molecules and the one at lower frequency to that of the monomers.

Solvent effect on the N—H and C=O absorption frequencies.—Richard and Thompson[7] have recorded the infra-red spectra of some amides in dioxane and acetonitrile, but their attention was mainly confined to the study of C=O stretching frequency and sometimes to the N—H deformation bands. The N–H stretching, N—H deformation and C=O stretching frequencies of the amides in donor solvents as recorded by the authors are given in Table I. From these observations it is evident that:

(i) The band at 3535 cm.$^{-1}$ that could be recorded in formamide in solutions of chloroform or a similar band in other primary amides is absent in the spectra of the same amide in donor solvents.

(ii) In the region of N—H stretch of these primary amides only two strong bands could be recorded in dioxane and acetonitrile together with a weak shoulder at 3210 cm.$^{-1}$ in each case. The frequencies of the strong bands are

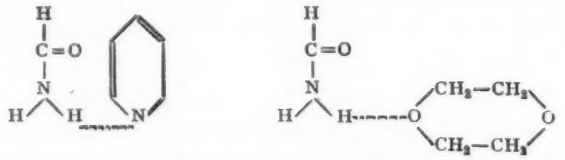
intermediate between the values of the pure amides and of the monomers in solutions of chloroform.

(iii) The band at 3210 cm.$^{-1}$ is very weak even at relatively high concentrations in these solutions and is altogether absent in solutions of pyridine in which the N—H stretching frequencies have even smaller values than those of the corresponding absorption bands of the associated molecules.

(iv) The N—H deformation frequencies in the donor solvents have an intermediate value of the frequencies of the same band in pure primary amides and in solutions of chloroform. This band is weaker in donor solvents compared to the one in solutions of chloroform and with increasing dilution it becomes very feeble in solutions of pyridine.

(v) The frequency of C=O stretching absorption of the amides which has only one value—in dilute solutions—shifts to a slightly higher value in dioxane than in other solvents.

The appearance of a single absorption band for C=O stretch in the donor solvents with a frequency equal to that of the monomers is an indication of the fact that at the concentrations considered the intermolecular association in the amides through N—H....O=C breaks down to a considerable extent. But the simultaneous reduction in the frequencies of the N—H stretch and increase in those of N—H deformation, compared to the corresponding monomer frequencies in chloroform, indicate that the donor groups of the solvents are associating with the amino group of the monomer amides as indicated below:



The shifts in the N—H stretching and deformation bands are highest in solutions of pyridine indicating the formation of relatively strong hydrogen bonds in this solvent.

The shifts of the N—H stretch of the N-methyl formamide in the donor solvents are similar to those of the primay amides.

The amide II band in the infra-red spectrum of N-methyl formamide is atl 546 cm.$^{-1}$, and in solutions of chloroform, it shifts to 1486 cm.$^{-1}$ and a weak peak could still be recorded at 1546 cm.$^{-1}$ even at low concentrations. The corresponding peaks in solutions of dioxane and pyridine are at 1546 and 1534 cm.$^{-1}$ and in acetonitrile, they are at 1546 and 1531 cm.$^{-1}$

The amide III band of N-methyl formamide at 1248 cm.$^{-1}$ in infra-red shifts to 1203 in carbon tetrachloride, to 1225 in acetonitrile, to 1222 in dioxane and to 1242 cm.$^{-1}$ in pyridine. The same band in Raman spectrum at 1243 cm.$^{-1}$ shifts to 1233 cm.$^{-1}$ in acetonitrile and to 1257 cm.$^{-1}$ in water. The shifts in the Raman lines are indicated in Plate II. These shifts in the case of amide II and III bands of N-methyl formamide in the donor solvents are in agreement with similar results obtained in case of N—H deformation bands of the primary amides. It is of interest to note that in mixtures of water, the Raman frequency of the amide III band has a value higher than that of even the associated molecules.

Hydrogen bond formation.—In strong solutions of N-methyl formamide in dioxane, two prominent peaks associated with C=O band at 1667 and 1695 cm.$^{-1}$ are recorded. With the increase of dilution the peak at 1667 cm.$^{-1}$ which is assigned to C=O stretch of the associated molecules gets weakened and finally at molar concentration of 0·13, only one band that of the monomer could be recorded. This indicates that the amide dissociates considerably at this concentration. In case of acetamide and benzamide as well, the concentrations of the amide in dioxane were so chosen as to give a single C=O stretching absorption band corresponding to those of the monomers. Phenol, in known ratios by volume, was added to each of these solutions of amides in dioxane and the infra-red spectrum of C=O band of each amide was recorded by keeping in the reference beam a solution of dioxane and phenol taken in the same ratio by volume. In this way dioxane and phenol were compensated for. The frequency of C=O band of the amide recorded in this way decreases gradually with increasing content of the phenol. These observations are given in Table IV.

TABLE IV

Variation in the frequency of C=O stretching absorption bands of amides in dioxane when mixed with penol

Amide	Mol. conc.	Frequency C=O stretch in dioxane (cm.$^{-1}$)	Frequency of C=O band in dioxane mixed with phenol			
			4 : 1	2 : 1	1 : 1	1 : 2
N-methyl formamide	0·13	1695	1695 1674	1671	1667	1667
Acetamide ..	0·11	1689	1672	1669	1666	1664
Benzamide ..	0·10	1686	1674	1671	1668	1666

When the proportion of the amide in solution of dioxane to phenol was as low as 4 : 1 by volume—in case of N-methyl formamide—the C=O band shifted to 1674 cm.$^{-1}$ and a weak shoulder was present at 1695 cm.$^{-1}$ which was the unmodified frequency. The presence of this frequency indicates that only a portion of the monomer molecules have formed hydrogen bonds with phenol. But in acetamide and benzamide the C=O band of the diminished frequency alone could be recorded, even when the ratio of the mixture to phenol was 4 : 1. With the increasing content of the phenol, the unmodified frequency disappeared completely and in case of all the amides studied the bands with modified frequency show a gradual decrease in their values. When the mixture to phenol ratio is as high as 1 : 2, the bonded C=O frequency in the presence of phenol is almost the same as that of the associated molecules.

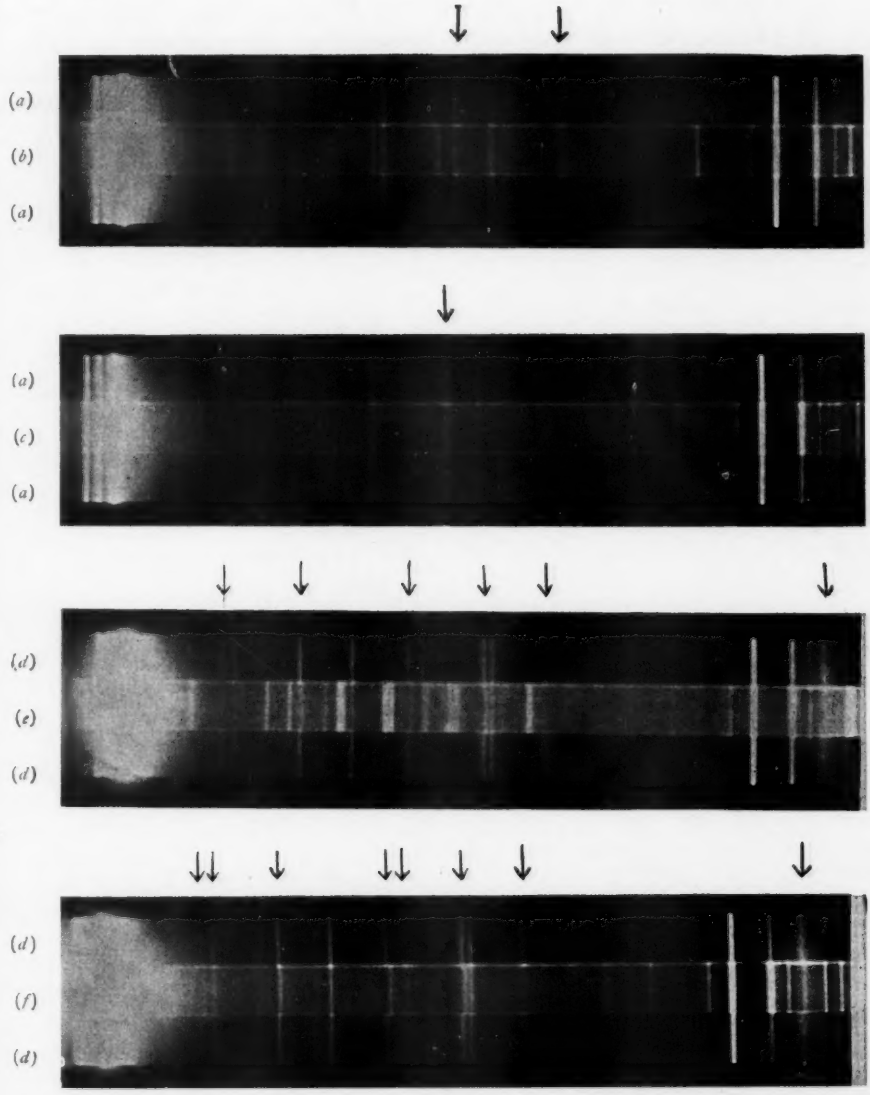
The Raman frequencies in solvents.—The C=O stretching frequency of N-methyl formamide at 1653 cm.$^{-1}$ shifts by 18 cm.$^{-1}$ towards higher value in mixtures of acetonitrile. This indicated considerable dissociation of the molecules, but the same frequency remains unchanged in solutions of water.

The Raman spectra of dimethyl formamide in mixtures of phenol and water show considerable shifts in as many as eight lines and these are indicated by arrows in Plate II. The frequencies of the pure amide at 354, 405, 666, 987, 1094, 1407, 1664 and 2945 cm.$^{-1}$ have shifted to 360, 410, 672, 998–1004, 1099–1104, 1418, 1657–1652 and 2953 cm.$^{-1}$ in solvents of phenol and water. The diminution of the C=O frequency of the amide in mixtures of phenol and water is due to the formation of hydrogen bond. This results in the weakening of the C=O bond and has secondary effects on the adjoining linkages resulting in the variation of the corresponding frequencies.

V. SUMMARY

The infra-red spectra of primary and secondary amides have been recorded in solutions at various concentrations with particular reference to 3 μ region. The apparent molecular extinction coefficients of various absorption bands in this region have been calculated at different concentrations and spectroscopic evidence is obtained for their dimeric manifestation in solutions. This method enabled the authors to assign the N—H asymmetric and symmetric stretching vibrations of the monomer and the associated molecules on a quantitative basis. The C=O stretch and the N—H in-plane deformation frequencies of monomer and associated molecules have also been assigned.

The effect of donor solvents on the frequencies of the amino and carbonyl bands has been investigated. It is observed that C=O frequencies of these amides in donor solvents are either the same or slightly higher than those of



Raman spectra of: (*a*) N-methyl formamide. (*b*) N-methyl formamide in acetonitrile 1:1 by volume. (*c*) N-methyl formamide in water 1:2 by volume. (*d*) Dimethyl formamide. (*e*) Dimethyl formamide in phenol 1:2 by volume. (*f*) Dimethyl formamide in water 1:4 by volume.

the same amides in solutions of chloroform, but the N—H stretching frequencies in the same donor solvents are less, the N—H deformation frequencies more, than the frequencies of the corresponding linkages in solutions of chloroform. These results are explained on the basis that the primary and the secondary amides dissociate in donor solvents and then the donor group of the solvents forms hydrogen bond with the amino group of the amide in the monomeric state. The C=O frequency of these amides in solutions of dioxane in the presence of phenol was studied and its diminution is accounted for as due to hydrogen bond formation. The Raman spectra of N-methyl formamide and dimethyl formamide and in various solvents have been recorded. Shifts observed in a number of Raman lines of these substances in mixtures are explained.

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ELECTRICAL OSCILLATIONS IN A CONSTRICTED D.C. COLD-CATHODE GLOW DISCHARGE WITH A THREE ELECTRODE SYSTEM

By Dr. V. T. Chiplonkar and P. K. Naik

(*Physics Department, Institute of Science, Bombay*)

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§ 1. The generation of electrical oscillations (in the L.F. Kc./s. range) in the plasma region of a cold-cathode glow discharge, has been associated, according to the hypothesis of Donahue and Dieke[1] with the formation of an electron trap, as a result of a maximum in the space potential in this region. According to Labrum and Bigg[2] a part of the oscillations may be due to a Barkhausen-Kurz type of oscillation of the electrons about the potential maximum when it is boosted up by the constriction of the discharge to the required extent. As the constriction is a function of the discharge current (*vide infra*) the suggestion would provide the necessary connection between the oscillations and the discharge current which has been observed experimentally.

In order to experimentally verify these suggestions we have investigated the production of the electrical oscillations in a cold-cathode D.C. glow discharge provided with a three electrode system of the type that obtains in the "Philips Ionisation Gauge". By giving appropriate voltages to the electrodes a potential maximum (or minimum) could be created and the conditions thus made favourable for the generation of the Barkhausen-Kurz type of oscillations of the electrons (or the ions).

§ 2. The discharge tube used was 30 mm. in diameter and was provided with central electrode A of moulded Aluminium (diameter 29 mm.), provided with a central opening. The outer electrodes B were of the same diameter and were symmetrically placed at a distance of 65 mm., on either side of the central electrode A. Observations were taken for discharge in Air (pressure range = 75–300 microns) and in Hydrogen (pressure range = 140–2,200 microns) for discharge currents between 0–10 mA., using gas-streaming. The electrical oscillations in the earthed discharge current were detected with the help of a C.R.O. in the L.F. region and an absorption wavemeter coupled with a capacitor probe for the H.F. range (ref. Chiplonkar and Mangaly[3]),

Observations with the central electrode as the anode under the various conditions of the pressure and the current showed that no oscillations were to be observed, either for discharge in Air or Hydrogen. The experimental investigations reported in this paper were taken only with the central electrode as the cathode.

The observations for Air were taken for three different sizes of the opening in the central electrode, *viz.*, A_1 (diameter = 10 mm.), A_2 (diameter = 20 mm.) and A_3 (diameter = 27 mm.). Visual observations showed that for large values of the current the discharge was of the constricted type which changed over into the uniform type at a critical value i_r of the current when it was gradually reduced. Photographs 1 and 2 show the appearance of the discharge in these two types. i_r is found to depend on the pressure and the size of the opening in the central electrode (*vide* Table I).

The disappearance of the constriction at i_r was accompanied in some cases by a sharp change in the V–i characteristics as seen in (Fig. 3) for p = 125–250 microns.

It is interesting to note that the change $\triangle V_c$ in the voltage at i_r is a function of the pressure (*vide* Table II).

The constriction of the discharge channel near the cathode, as visually observed, was found to increase as the current was reduced. This was confirmed by determining the radial distribution in the intensity of the discharge channel (at a fixed distance $Z = 5$ mm. from the cathode) with a photomultiplier (*see* Fig. 4).

§ 3. The electrical oscillations observed in these experiments were usually in the form of electrical noise. A typical photograph of the C.R.O. pattern observed is shown in Fig. 5. These oscillations were only observed in the constricted regime of the discharge near the transition stage when the discharge was undergoing a transformation from the constricted to the uniform type (*vide* Fig. 3). The observations showed the presence of an upper cut-off current i_c beyond which the oscillations were quenched. i_c shows a variation with the pressure and the size of the opening in the central electrode (*vide* observations in Table I) which is similar to the variation shown by i_r under these conditions, suggesting a close relationship between them. The value of i_c may therefore be taken to indicate the value of the discharge current which corresponds to the minimum magnitude of the constriction necessary for the generation of the oscillations (*vide* Labrum and Bigg[2]).

TABLE I

Central cathode discharge in air

i_c = upper cut-off current for oscillations. i_r = lower cut-off for constriction.

Pressure in microns	Central electrode A_1 (opening diameter = 10 mm.)			Central electrode A_2 (opening diameter = 20 mm.)			Central electrode A_3 (opening diameter = 27 mm.)		
	i_r mA.	i_c mA.	Nature of oscillations	i_r mA.	i_c mA.	Nature of oscillations	i_r mA.	i_c mA.	Nature of oscillations
75	..	..	No oscillations, no constriction	..	..	No oscillations, no constriction	..	..	No oscillations, no constriction
100	..	..	,,	..	..	,,	..	..	,,
125	5·50	5·50	Noise	3·30	3·90	Noise	..	..	..
150	3·50	3·50	,,	..	..	..	2·00	2·00	Noise
175	3·00	3·20	,,	1·30	1·60	Noise	..	..	..
200	3·00	3·20	Noise+Monofrequency (50 Kc./s.)	..	..	..	1·10	1·10	Noise
250	2·50	2·70	Noise	0·90	1·00	Noise	0·50	0·50	,,
300	1·75	2·10	Noise+Monofrequency (50 Kc./s.)	..	..	No oscillations, constriction present throughout	..	..	No oscillations, constriction present throughout
400	..	..	..	..	..	,,	..	..	,,
500	..	..	..	..	..	,,	..	..	,,

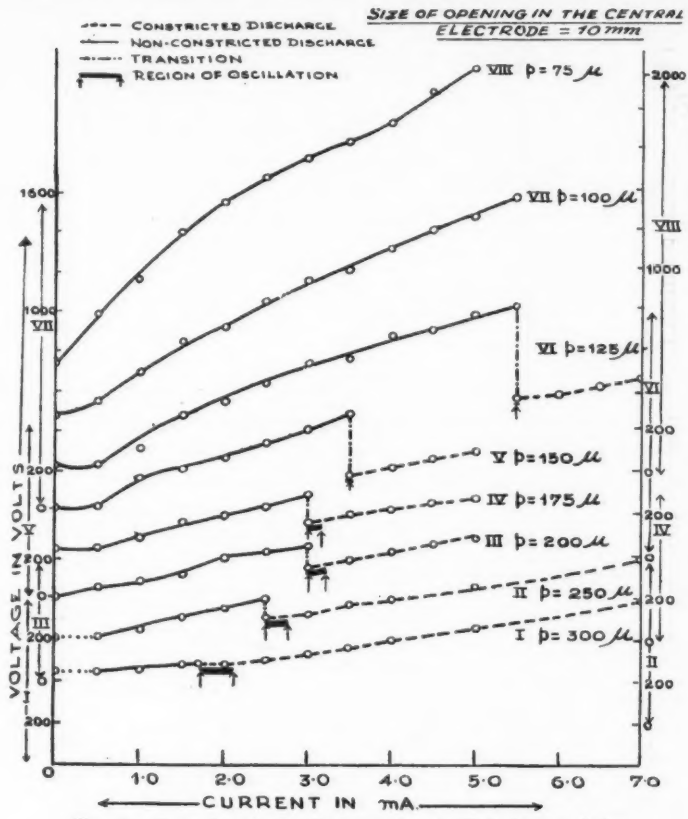

FIG. 3. Central cathode discharge in air V–*i* characteristics.

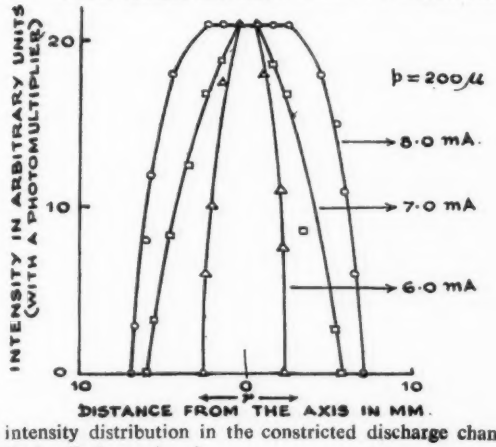

FIG. 4. Radial intensity distribution in the constricted discharge channel in the cathode region. Central cathode discharge in air.

TABLE II

Central cathode (A_1) discharge in air

V_{cr} = Voltage at i_r. ΔV_c = Change in voltage.

p	V_{cr}	ΔV_c	$\frac{\Delta V_c}{V_{cr}}$
Microns	Volts	Volts	
125	740	550	0·74
150	575	300	0·52
175	550	125	0·23
200	540	85	0·16
250	500	65	0·13
300	475	0	0·00

§4. In contrast to the observations obtained for the discharge in Air, the oscillations observed in the case of Hydrogen were of the monofrequency type, although they were also to be observed near the transition range between the constricted and the uniform type of the discharge (*vide* Fig. 6). It may

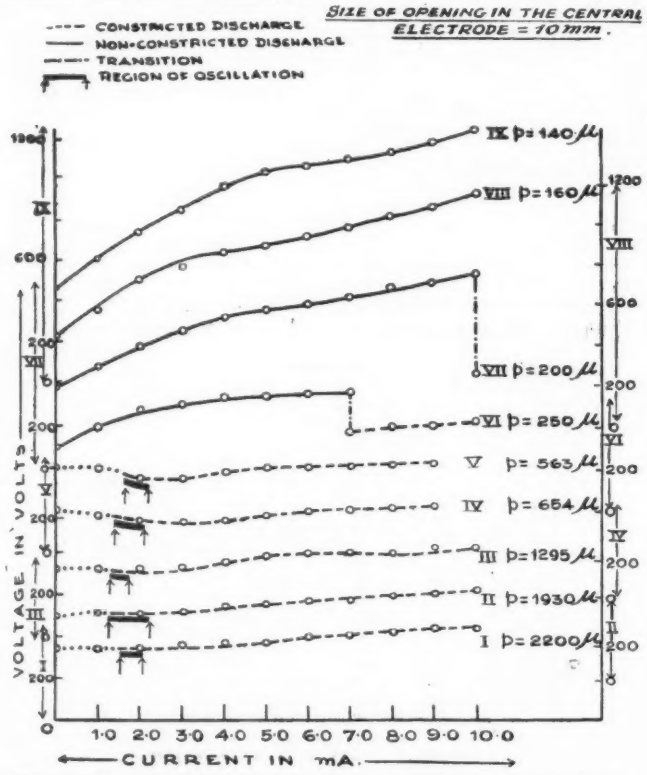

FIG. 6. Central cathode discharge in hydrogen V–i characteristics.

be pointed out that for $p = 200$ and 250 microns, no oscillations were observed even though the transition was accompanied by a sharp and discontinuous change in the V–i characteristics. These reuslts show that a sharp change in the V–i characteristics and/or a transformation of the discharge is not a sufficient criterion for the generation of the oscillations. At the same time it should be remarked that the oscillations were observed only during the transition stage both in the case of the discharge in Air and Hydrogen.

Table III shows the variation of i_c, i_r with pressure for the central cathode discharge in Hydrogen with A_1 as the central electrode.

TABLE III

Central cathode (A_1) discharge in hydrogen

i_c = Upper cut-off current for oscillations. i_r = Lower cut-off for the constriction.

p microns	i_r mA.	i_c mA.
140	No constriction	..
160	,,	..
200	10·00	..
250	7·00	..
560	1·55	2·10
650	1·30	2·10
1300	1·20	1·60
1930	1·15	2·25
2200	1·35	2·05

Table IV shows the variation of frequency and the amplitude (as measured by the C.R.O.) of the oscillations with current at the different pressures. A typical photograph of the C.R.O. pattern observed under these conditions is shown in Fig. 7.

It should be mentioned that for discharge in Air and Hydrogen under these conditions (1) no high frequency components were observed (Chiplonkar

TABLE IV

Central cathode (A_1) discharge in hydrogen

$p = 1930$ microns		Amplitude in arbitrary units
i mA.	f Kc./s.	
$2{\cdot}25 = i_0$	..	..
2·20	100	12
2·00	100	15
1·75	100	15
1·50	75	13
1·20	75	8
$1{\cdot}15 = i_r$	..	..
$p = 650$ microns		
$2{\cdot}10 = i_0$	..	..
2·05	150	12
1·90	125	14
1·80	100	14
1·70	100	13
1·60	100	13
1·50	100	13
1·40	75	12
1·35	50	12
$1{\cdot}30 = i_r$	..	..
$p = 560$ microns		
$2{\cdot}10 = i_0$	..	..
2·05	90	14
1·90	90	13
1·85	90	13
1·80	130	12
1·75	130	12
1·70	115	10
1·60	115	8
$1{\cdot}55 = i_r$	..	..

Table V shows the dependence of the frequency on the pressure.

TABLE V

Central cathode (A_1) discharge in hydrogen

i mA.	p microns	f Kc./s.
1·80	2200	225, 110
..	1930	100*
..	1300	..
..	650	100
..	560	130
1·60	2200	225
..	1930	85*
..	1300	..
..	650	100
..	560	115
1·50	2200	225*
..	1930	75
..	1300	170
..	650	100
..	560	..

* Estimated values.

and Mangaly[3]), (2) no electrical oscillations or the constriction was observed with the central electrode as the anode.

§ 5. The results reported here do not therefore give experimental evidence in favour of the hypothesis of Labrum and Bigg. The fact that the oscillations have been observed only in the case of the discharge with central cathode and that too in a narrow current range, restricted to the transition stage, leads to the supposition that the oscillations reported here may have a

different origin (*e.g.*, an instability in the cross-section of the discharge channel) and may not be of the same type as observed by Donahue and Dieke,[1] Pilon,[4] Chiplonkar and Mangaly.[3] The following points of similarity and difference between the two types of oscillations may be emphasised.

(i) The existence of a cut-off current and its variation with p are similar.

(ii) The frequency of the oscillations reported here is sensitive to the discharge parameters p and i, although not to the extent as observed in the other type.

(iii) In the case of discharge in Hydrogen (except for $p = 2{,}200$ microns, $i = 1{\cdot}80$ mA.) only *monofrequency* oscillations were observed for all the pressures; the different frequency modes were not obtained as in the Previous case.

We thank Dr. R. K. Asundi for useful discussions and suggestions.

SUMMARY

The generation of the electrical oscillations has been studied for a D.C. cold cathode glow discharge with three electrodes in Air ($p = 75$–300 microns) and Hydrogen ($p = 140$–$2{,}200$ microns) for currents 0–10 mA. with

Case I: Central electrode as cathode.

Case II: Central electrode as anode.

Oscillations were observed only in Case I over a narrow current range associated with a constricted type of discharge. The oscillations were in the form of the electrical noise for Air and of the monofrequency coherent type (75–225 Kc./s.) for Hydrogen. No oscillations were observed for Case II.

There was no evidence for the Barkhausen Kurz type of oscillations of electrons (or ions) about the potential maximum (or minimum) in the plasma region as suggested by Labrum and Bigg.

Observations suggest that the oscillations observed may be due to an instability in the cross-section of the discharge channel.

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FIG. 1. Constricted type discharge in Air. $p = 175\,\mu$, $i = 5{\cdot}00\,m$A., Vc = 675 Volts. $d = 0{\cdot}7$ cm., d = length of cathode dark space.

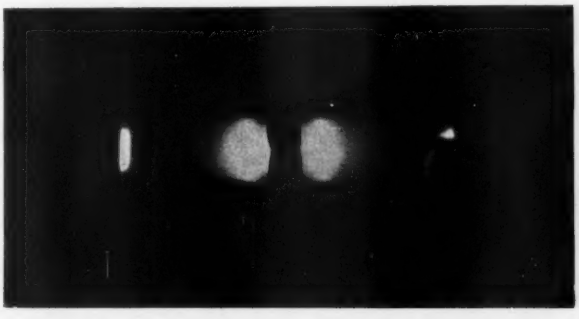

FIG. 2. Uniform type discharge in Air. $p = 175\,\mu$, $i = 2{\cdot}50\,m$ A., Vc = 625 Volts, $d = 0{\cdot}7$ cm.

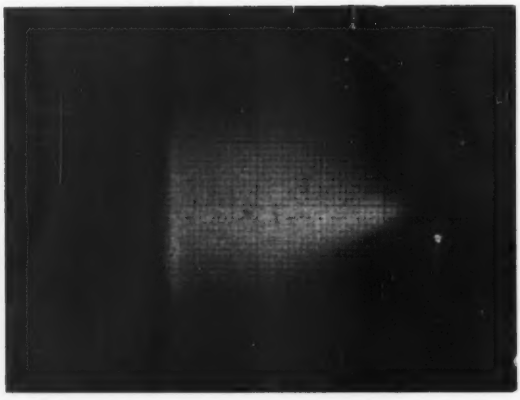

FIG. 5. Electrical noise for central cathode discharge in Air. $p = 125\mu$, $i = 5{\cdot}50\,m$A, Vc = 740 volts.

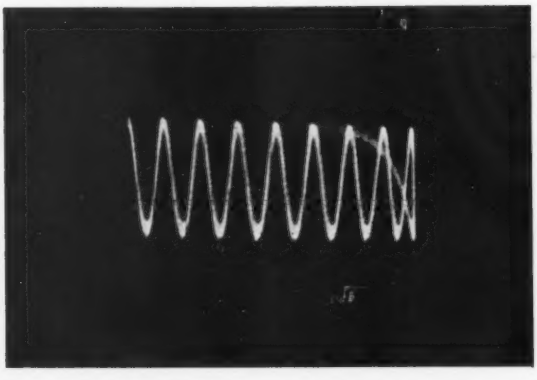

FIG. 7. Monofrequency oscillations for central cathode discharge in Hydrogen. $p = 1300\,\mu$, $i = 1{\cdot}30\,m$A., Vc = 325 volts, $f = 125$ kcs.

RAMAN SPECTRA OF ORGANIC COMPOUNDS

Part II. Methyl Borate

By K. Krishnan

(*Department of Physics, Indian Institute of Science, Bangalore-12*)

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1. Introduction

In continuation of the earlier work (Krishnan, 1961) the author has recorded the Raman spectrum of methyl borate $B(OCH_3)_3$ using ultra-violet excitation. This substance is a liquid at ordinary temperatures. The Raman spectrum of methyl borate was investigated by Joglekar and Thatte (1936), Ananthakrishnan (1936), Milone (1936), Kahovec (1938, 1939) and by Becher (1954). They had employed the 4046 and 4358 excitation. The maximum number of Raman lines reported so far is fifteen. Ananthakrishnan and Becher investigated the polarisation characteristics of the Raman lines also though their results were not in complete agreement.

The liquid used in the present investigation was pure Kahlbaum's sample. Since the liquid got easily decomposed due to the action of atmospheric water vapour, the Wood's tube containing the sample was kept carefully sealed. The liquid exhibited traces of fluorescence. The spectrum was recorded with a Hilger medium quartz spectrograph using Ilford Zenith Astronomical plates, the slit-width used being 0·02 mm. Exposures of about 40 hours were given to record a reasonably intense picture.

2. Results

An enlarged photograph of the Raman spectrum of methyl borate is reproduced in Fig. 1 on Plate V, along with its microphotometer record. The frequency shifts of the Raman lines are marked in the microphotometer tracing. Thirty-four Raman lines have been recorded and the frequency shifts have been entered in column 1 of Table I. The figures given within brackets represent the visual estimates of their intensities. The intense 'wing' extending up to 110 wavenumbers from the exciting line is a new feature of the recorded spectrum. In column 2 of Table I are given the frequency shifts reported by Ananthakrishnan (1936). The frequencies corresponding

to the prominent maxima in the infra-red absorption spectrum of methyl borate taken by Becher (1954) are given in column 3 of Table I.

3. DISCUSSION

(*a*) *Structure of the molecule.*—From electron diffraction studies Bauer and Beach (1941) have definitely established that the boron and the three oxygen atoms of methyl borate are in one and the same plane with $B\hat{O}C = 113°$. On this basis one can have two possible structures for the methyl borate molecule. These two structures have the respective point-group symmetries C_3 and C_{3h}. The point-group C_3 could be eliminated as some of the vibrational modes which appear in Raman effect are not recorded in infra-red absorption and *vice versa*. Hence the only possible structure for methyl borate is the one having the symmetry of the point-group C_{3h}. The structure is indicated in Fig. 2. This conclusion is also supported by the investigations of Becher (1954).

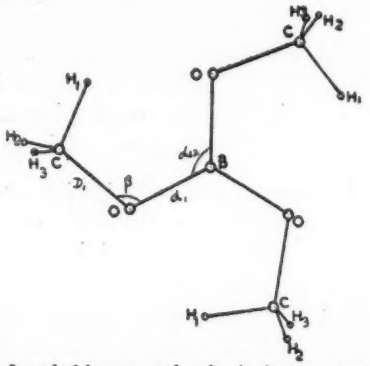

FIG. 2. The structure of methyl borate molecule: hydrogen atoms 1 are in the BO_3C_3 plane. The hydrogen atoms 2 and 3 are situated above and below the BO_3C_3 plane symmetrically.

(*b*) *Vibrational assignments.*—A molecule having the symmetry C_{3h} will have four species of vibrations—A′, A″, E′ and E″. Of these A′, E′ and E″ are active in Raman effect and A″ and E′ are infra-red-active. Of the Raman-active species A′ will give rise to polarised Raman lines, while the other two species produce depolarised Raman lines. Since $B(OCH_3)_3$ molecule contains sixteen atoms, it will have 42 fundamental modes of vibration distributed among the various species as follows:

$$8A' + 6A'' + 9E' + 5E'',$$

i.e., there will be 28 distinct fundamental frequencies. Of these 10 are due to the internal vibrations of the BO_3C_3 group and the rest due to the vibra-

tions of the CH_3 groups. Hence from a knowledge of the polarisation of the Raman lines and from the activity of the various frequencies, a satisfactory vibrational assignment could be made. Unfortunately only a trial polarisation picture was taken, and this is used in conjunction with Ananthakrishnan's data for making the assignments. The latter are indicated in column 4 of Table I. Column 5 of the same table gives the species of the vibrations.

Regarding the vibrations of the CH_3 groups, Ananthakrishnan observed six and the present author seven Raman lines in the C–H stretching region, whereas theoretically only five Raman lines—three polarised and 3 depolarised —are expected. Of the seven Raman lines observed, five are definitely polarised. The existence of a large number of Raman lines in this region could only be explained on the basis of Fermi resonance between the C–H stretching frequencies and the overtones of the C–H bending frequencies.

In the C–H bending region also five Raman lines—two polarised and three depolarised—are expected. But only two Raman lines—one very weak at about 1390 $cm.^{-1}$ and another strong and broad at 1465 $cm.^{-1}$, both depolarised—are observed. There is a diffuse background extending over 200 wavenumbers. The other C–H bending frequencies might have overlapped with the one at 1465 $cm.^{-1}$

Of the CH_3 rocking frequencies the one at 1176 $cm.^{-1}$, which has a corresponding infra-red frequency, is definitely depolarised and has to be assigned to the species E′. The other assignments are indicated in Table I.

Restricting oneself to the BO_3C_3 group, one should expect to get eight Raman lines and two infra-red absorption bands not coinciding with the Raman lines below 1500 $cm.^{-1}$ Of these three should belong to the group A′ and hence should be polarised and the other five should be depolarised. Also the in-plane vibrations, *viz.*, those belonging to the species E′, should be in general, stronger than the out-of-plane vibrations, *viz.*, those belonging to the species E″. In the case of the BO_3C_3 group, there should be four vibrations belonging to species E′ and one belonging to E″. On this basis the assignments indicated in Table I are made. For the species A′ and E′ our assignments are in complete agreement with those of Becher (1954). However, a weak line at 575 $cm.^{-1}$ observed by Becher has been assigned to species E″. This line is not present in the spectrum recorded by the author. The depolarised Raman line appearing weakly at 546 $cm.^{-1}$ has therefore been assigned to E″ instead.

There are two vibrations belonging to the species A″, which are infra-red-active. One frequency has been given by Becher for the BO_3 out of plane

deformation at 664 cm.$^{-1}$ The other frequency, *viz.*, the BOC out of plane bending could be at 575 cm.$^{-1}$ This assignment is quite tentative since there are no infra-red data below 600 cm.$^{-1}$

There remain two more frequencies to be identified, which arise due to the twisting of the CH_3 group. The Raman-active CH_3 twisting frequency can be identified with the weak Raman line at 473 cm.$^{-1}$ The other infra-red-active degenerate CH_3 twisting vibration is arbitrarily taken to give a frequency of 250 cm.$^{-1}$

TABLE I

Raman spectrum of methyl borate

	Author	Anantha-krishnan	Becher (I.R.)	Assignment	Species
	0–110	..	..	Wing	..
1.	200 (12)	..	197	..	BOC deformation	E′
2.	318 (12)	..	320	..	BOC deformation	A′
3.	473 (2)	..	..	..	CH_3 twisting	E″
4.	524 (8)	..	526	..	BO_3 deformation	E′
5.	546 (1)	..	..	..	BOC deformation out of plane	E″
	..	..	..	664	BO_3 out of plane deformation	A″
6.	673 (1)	..	..	..	200 + 473	E′+E″
7.	726 (18)	..	728	..	B–O stretching	A′
8.	774 (12)	..	..	776	318 + 473	A′+E″
9.	815 (1)	..	..	815	524 + 318	A′+E′
10.	920 (1 *b*)	..	..	923	726 + 200	A′+E′
11.	1030 (16)	..	1030	1029	C–O stretching	E′
12.	1114 (10)	..	1117	..	C–O stretching	A′
13.	1175 (10)	..	1174	1176	CH_3 Rocking	E′

TABLE I (*Contd.*)

	Author	Anantha-krishnan	(I.R.)	Assignment	Species
14.	1224 (1) ..	..	..	„	E″
	..	..	1247	„	A″
15.	1287 (1) ..	..	..	„	A′
16.	1335 (1) ..	..	1347	B–O stretching	E′
17.	1390 (1 *b*) ..	..	1392	CH_3 bending	E′
18.	1465 (15 *b*) ..	1460	..	„	E″
	..	..	1511	„	A″
19.	2060 (1) ..	..	..	2 × 1030	2E′
20.	2139 (0) ..	..	2150	1030 + 1114	A′+E′
21.	2183 (0) ..	..	..	1030 + 1175	E′+E′
22.	2227 (0) ..	..	2220	2 × 1114	2 A′
23.	2330 (1) ..	..	..	2 × 1175	2 E′
24.	2528 (0) ..	..	2510	1347 + 1175	E′+E′
25.	2617 (5 *b*) ..	2614	2610	1465 + 1175	E′+E″
26.	2812 (16) ..	..	..	CH_3 stretching	..
27.	2838 (16) ..	2838	..	CH_3 stretching	A′
28.	2870 (20) ..	2870	2875	„	E′ ?
29.	2905 (16) ..	2910	..	„	..
	..	..	2925	„	A″
30.	2942 (20) ..	2940	..	„	A′
31.	2974 (16) ..	2974	2960	„	E′
32.	2996 (16) ..	2988	..	„	E″
33.	3480 (1) ..	..	..	2942 + 524	A′+E′
34.	3572 (1) ..	..	..	2870 + 726	A′+E′

There are a number of faint Raman lines which could be explained only as combinations and overtones of the fundamental frequencies and their assignments are also included in Table I. The fairly strong Raman line at about 776 cm.$^{-1}$ may be the combination 318 + 473 cm.$^{-1}$ which has increased in intensity because of its nearness to the intense B–O stretching frequency at 726 cm.$^{-1}$ For the symmetry C_{3h} the following combinations are active in the Raman effect: $a' + e'$, $a' + e''$, $a'' + e'$, $a'' + e''$ and $e' + e''$. The combining species of the various combination lines are indicated in column 5 of Table I.

(*c*) *Calculation of force constants for methyl borate.*—Since a group theoretical analysis of the whole molecule of $B(OCH_3)_3$ will involve 8th and 9th degree equations which could not be solved here, the molecule is treated as a planar XY_3Z_3 one the CH_3 group being considered as a single unit. This molecule will have 10 distinct fundamental frequencies distributed among the various species as follows:

$$3A' + 2A'' + 4E' + 1E''.$$

Also, since there is no infra-red data below 600 cm.$^{-1}$, the out-of-plane motions, *i.e.*, species A″ and E″ are not treated here. Wilson's (1939, 1941) F–G matrix method is used for calculating the force constants.

Internal co-ordinates.—The internal co-ordinates chosen for this problem are Δd_1, Δd_2, Δd_3; ΔD_1, ΔD_2 and ΔD_3, the changes in B–O and O–C distances respectively, and $\Delta\alpha_{12}$, $\Delta\alpha_{23}$, $\Delta\alpha_{31}$; $\Delta\beta_1$, $\Delta\beta_2$ and $\Delta\beta_3$, the changes in OBO and BOC angles. These are indicated on Fig. 2. As there are 12 internal co-ordinates, 12 symmetry co-ordinates can be constructed from these. Of these only eleven are genuine, and so one co-ordinate must be redundant. This is in the species A′. The symmetry co-ordinates for the various species are:

Species A′

$$R_1 = \frac{1}{\sqrt{3}}(\Delta d_1 + \Delta d_2 + \Delta d_3)$$

$$R_2 = \frac{1}{\sqrt{3}}(\Delta D_1 + \Delta D_2 + \Delta D_3)$$

$$R_3 = \frac{1}{\sqrt{3}}(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)$$

Species E'

$$R_{4a} = \frac{1}{\sqrt{6}}(2\Delta d_1 - \Delta d_2 - \Delta d_3)$$

$$R_{4b} = \frac{1}{\sqrt{2}}(\Delta d_2 - \Delta d_1)$$

$$R_{5a} = \frac{1}{\sqrt{6}}(2\Delta D_1 - \Delta D_2 - \Delta D_3)$$

$$R_{5b} = \frac{1}{\sqrt{2}}(\Delta D_2 - \Delta D_3)$$

$$R_{6a} = \frac{1}{\sqrt{6}}(2\Delta \alpha_{23} - \Delta \alpha_{31} - \Delta \alpha_{12})$$

$$R_{6b} = \frac{1}{\sqrt{2}}(\Delta \alpha_{31} - \Delta \alpha_{12})$$

$$R_{7a} = \frac{1}{\sqrt{6}}(2\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3)$$

$$R_{7b} = \frac{1}{\sqrt{2}}(\Delta \beta_2 - \Delta \beta_3).$$

Using these co-ordinates the elements of the G-matrices can be evaluated and are given below:

Species A':

$$G_{11} = \mu_0$$

$$G_{22} = \mu_0 + \mu_c$$

$$G_{33} = \frac{\mu_c}{D_0^2} + \mu_0\left[\frac{1}{D_0^2} + \frac{1}{d_0^2} - \frac{2\cos\beta}{d_0 D_0}\right]$$

$$G_{12} = \mu_0 \cos\beta$$

$$G_{13} = -\frac{\mu_0 \sin\beta}{D_0}$$

$$G_{23} = -\frac{\mu_0 \sin\beta}{d_0}.$$

Species E':

$$G_{44} = \mu_0 + \frac{3}{2}\mu_B$$

$$G_{55} = \mu_0 + \mu_c$$

$$G_{66} = \frac{3\mu_0}{d_0^2} + \frac{9\mu_B}{2d_0^2}$$

$$G_{77} = \frac{\mu_C}{D_0^2} + \mu_0\left[\frac{1}{d_0^2} + \frac{1}{D_0^2} - \frac{2\cos\beta}{d_0 D_0}\right] + \frac{3}{2}\frac{\mu_B}{d_0^2}$$

$$G_{45} = \mu_0 \cos\beta$$

$$G_{46} = \frac{3\sqrt{3}}{2}\frac{\mu_B}{d_0}$$

$$G_{47} = -\mu_0 \frac{\sin\beta}{D_0}$$

$$G_{56} = 0$$

$$G_{57} = -\mu_0 \frac{\sin\beta}{d_0}$$

$$G_{67} = 0$$

where d_0 = equilibrium B–O distance = 1·38 A, D_0 = equilibrium O–C distance = 1·43 A, $\beta = B\hat{O}C = 113°$, and the μ's are the inverse masses. μ_C is the inverse mass of the CH_3 group as a whole.

F-matrices.—Only a simple valence potential function is employed taking into account a few interaction terms. The F-matrices for the two species are then as follows:

Species A'

$$\begin{bmatrix} F_d + 2F_{dd} & 0 & 0 \\ 0 & F_D & 0 \\ 0 & 0 & d_0^2[F_\beta + 2F_{\beta\beta}] \end{bmatrix}$$

Species E'

$$\begin{bmatrix} F_d - F_{dd} & 0 & 0 & 0 \\ 0 & F_D & 0 & 0 \\ 0 & 0 & d_0^2 F_\alpha & 0 \\ 0 & 0 & 0 & d_0^2[F_\beta - F_{\beta\beta}] \end{bmatrix}$$

where the F's have the usual significance. The secular equation for each species is then separately got as $(FG - E\lambda) = 0$ where E is a unit matrix. Thus we get a cubic equation for the species A' and quartic one for the species E'. Using the frequencies 726, 1114 and 318 cm.$^{-1}$ for species A' and 1347, 1030, 524 and 200 cm.$^{-1}$ for species E' the force constants could be found by a method of successive approximations. They are found to be:

$F_d = 4{\cdot}579 \times 10^5$ dynes cm.$^{-1}$

$F_D = 5{\cdot}315 \times 10^5$ dynes cm.$^{-1}$

$F_\alpha = 0{\cdot}130 \times 10^5$ dynes cm.$^{-1}$

$F_\beta = 0{\cdot}527 \times 10^5$ dynes cm.$^{-1}$

$F_{dd} = -0{\cdot}088 \times 10^5$ dynes cm.$^{-1}$

$F_{\beta\beta} = 0{\cdot}037 \times 10^5$ dynes cm.$^{-1}$

(*d*) *Calculation of thermodynamic quantities.*—Since all the 42 fundamental frequencies of methyl borate could be identified, the statistical thermodynamic functions of the molecule could be computed following the methods outlined by Herzberg (1945) and Taylor and Glasstone (1946). These are given in Table II for temperatures from 300° K. to 1,000° K. The moments of inertia of the molecule are:

TABLE II

T° K.	$\frac{H_0 - E_0}{T}$	$\frac{F_0 - E_0}{T}$	S	C
300	16·315	61·840	78·152	28·352
400	20·363	67·100	87·459	36·562
500	24·367	72·083	96·448	43·957
600	28·177	76·897	105·071	50·268
700	31·703	81·426	113·127	55·608
800	34·989	85·927	120·913	60·143
900	37·998	90·240	128·235	63·966
1000	40·783	94·391	135·171	67·253

All the values are given in calories per mole per ° C.

$\frac{H_0 - E_0}{T}$ = Total heat capacity.

$\frac{F_0 - E_0}{T}$ = Total free energy.

S = Total entropy.

C = Total heat content.

$I_A = 561 \cdot 682 \times 10^{-40}$ gm./cm.^{2} (about the principal 3-fold axis)

$I_B = I_C = 280 \cdot 841 \times 10^{-40}$ gm./cm.^{2} (about axes in the molecular plane).

The error, introduced by the uncertainty in the BOC out-of-plane vibration frequency and CH_3 twisting frequency in the infra-red absorption, will be only very small. Table II has been calculated on the assumption that there is no free or hindered rotation of the CH_3 groups. In the liquid state at least there seems to be no evidence for free or hindered rotation of the methyl groups.

4. SUMMARY

The Raman spectrum of methyl borate has been recorded using mercury λ 2537 excitation. Thirty-four Raman lines are recorded of which eighteen are reported for the first time. A complete vibrational assignment has been attempted by a comparison of the infrared and Raman spectra of methyl borate on the assumption that the molecular symmetry is C_{3h}. Using Wilson's F—G matrix method, the force constants for the in-plane vibrations of the BO_3C_3 part of the molecule have been calculated. Also, the entropy, heat content, heat capacity and free energy of the molecule have been evaluated from the spectroscopic data, on the assumption that the methyl groups exhibit no free or hindered rotation.

5. ACKNOWLEDGMENTS

The author has great pleasure in expressing his gratitude to Professor R. S. Krishnan for suggesting the problem and for many discussions. His thanks are also due to Dr. P. S. Narayanan for many helpful discussions.

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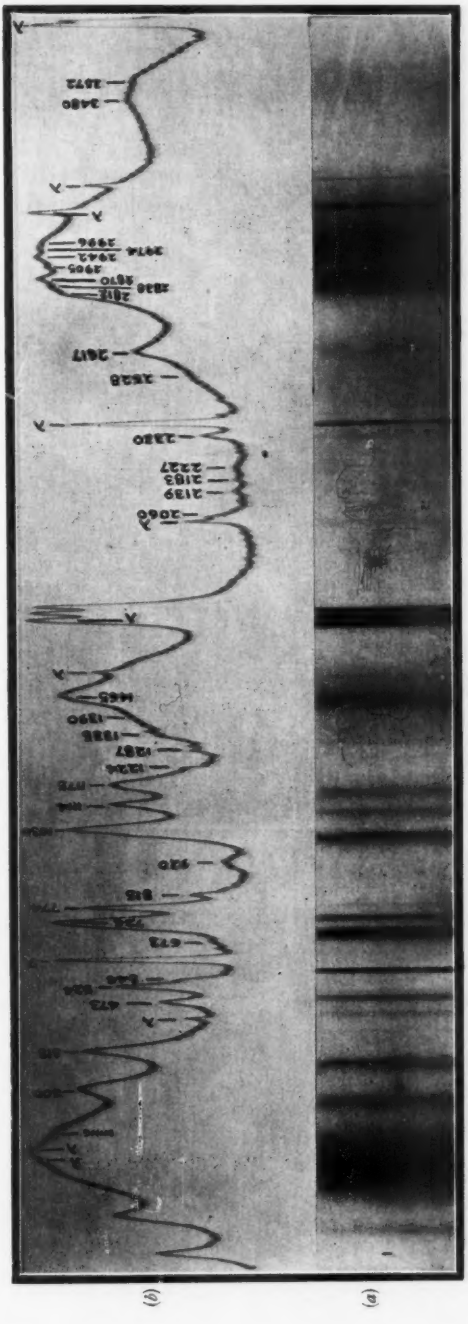

FIG. 1. (*a*) Raman spectrum of methyl borate taken with medium quartz spectrograph.
(*b*) Its microphotometer record.

CHEMICAL EXAMINATION OF THE LEAVES OF *RHODODENDRON CINNAMOMEUM*

By S. Rangaswami, F.A.Sc. and K. Sambamurthy

(*Department of Pharmacy, Andhra University, Waltair*)

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The results of the chemical examination of the leaves of *R. falconeri*, *R. nilagiricum* and *R. campanulatum* have been reported in earlier communications from these laboratories.[1-3] *R. cinnamomeum* is a tree growing in the Darjeeling region of the Himalayas. This is a distinct species which is likely to be confused with *R. arboreum*, but can be easily recognised by the dense rusty tomentum on the lower surface of the leaves. Further, the flowers of *R. cinnamomeum* are not so bright red as those of *R. arboreum*.

A survey of the literature showed that the plant has not been examined so far.

The powdered leaf was extracted with petroleum ether, chloroform and alcohol in succession. The petroleum ether extract yielded crystal mixtures which, by fractional crystallization followed by chromatography over alumina, could be separated into three components. One melting at 280–82° was identified as epifriedelanol. Another melting at 258–60° was identified as friedelin.[4-6] A minor component, m.p. 74–76°, was not examined further. The chloroform extract yielded ursolic acid. The alcohol extract, when examined as described in the experimental section, yielded quercetin and a minor component.

Ursolic acid and quercetin were identified by their properties and those of their acetates and by mixed melting points.

Friedelin has so far been reported to occur in only one Rhododendron species, *viz.*, *R. westlandii*.[7] The identity of the substance obtained in the present investigation was deduced from its properties and by the preparation of its 2:4-dinitrophenylhydrazone[8] and enol-benzoate[6] and by reduction to friedelan-3α-ol.[6]

The identity of epifriedelanol (friedelan-3 β-ol) was established by the preparation of its acetate and by oxidation to friedelin (m.p. and mixed m.p.).

EXPERIMENTAL

The coarsely powdered leaf (3 kg.) was extracted with petroleum ether, then with chloroform and then with alcohol in the cold using 3×8 l. of each solvent. These were followed by a single extraction with hot alcohol.

Petroleum ether extract.—The dark-green extract was concentrated to 250 ml. and left overnight at room temperature when a heavy crystalline material deposited. This was filtered and washed with warm petroleum ether (fraction A, 3 g.). The filtrate was further concentrated, the syrupy residue treated with hot acetone (150 ml.) and the mixture allowed to stand for a few days at room temperature, when crystals deposited along with some waxy matter. This was filtered and the wax washed off with warm acetone leaving behind fraction B (3 g.). The combined mother liquor, on removal of the solvent, yielded a dark-green residue (residue X, 76 g.) whose examination is described later.

Fractions A and B.—These two fractions had similar properties. They were united and crystallized from excess of chloroform, when clusters of colourless glistening plates slowly separated. These were filtered and recrystallized from chloroform, m.p. 280–82° (epifriedelanol, 2·8 g.; for characterisation *see* later). The residue (3 g.) from the combined mother liquor was chromatographed over alumina (90 g.) employing 200 ml. portions of solvents for elution. The course of the chromatogram is shown in Table I.

Fractions 1 and 2 were united and crystallized twice from benzene-acetone when colourless nodules were obtained, m.p. 74–76° (minor component, 0·15 g.).

Fractions 3 to 6 were united and crystallized twice from benzene, when long colourless needles were obtained, m.p. 258–60° (friedelin, 1·4 g.; for characterisation *see* later).

Fractions 7 to 9 were united and crystallized from chloroform as colourless plates, m.p. 278–80° (epifriedelanol, 0·4 g.).

Residue X (mentioned earlier) was saponified with 10% sodium hydroxide in benzene-alcohol (1 : 9) solution and the unsaponifiable matter (30 g.) was extracted in the usual way. It was dissolved in warm acetone (100 ml.) and left at room temperature for a week. The crystals that deposited were filtered, washed and recrystallized from chloroform, when colourless plates were obtained, m.p. 278–80° (epifriedelanol, 0·2 g.). $[\alpha]_D^{28} = +21{\cdot}1° \pm 2°$ ($c = 0{\cdot}824$ in chloroform). Mixed m.p. with epifriedelanol obtained above was undepressed. The rest of the unsaponifiable matter was rejected.

TABLE I

Fraction No.	Eluate	Residue	
		Weight in mg.	M.p. after a single crystallization
1.	Petroleum ether ..	7	70–72°
2.	Petroleum ether-benzene (19 : 1) ..	160	72–73°
3.	„ (9 : 1) ..	340	248–55°
4.	„ (4 : 1) ..	540	250–54°
5.	„ (1 : 1) ..	830	250–54°
6.	Benzene ..	210	254–56°
7.	Benzene-chloroform (19 : 1) ..	150	265–67°
8.	„ (9 : 1) ..	220	266–69°
9.	„ (4 : 1) ..	120	268–70°
10.	„ (1 : 1) ..	50	Amorphous
11.	Chloroform ..	20	„

Minor component.—M.p. 74–76°. No colour in the Salkowski or Liebermann-Burchard test or with tetranitromethane. $[\alpha]_D^{29} = +21{\cdot}2° \pm 3°$ ($c = 0{\cdot}6141$ in chloroform). Found: C, 82·4; H, 14·6. $C_{29}H_{60}O$ (probable formula) requires: C, 82·0; H, 14·2%.

Friedelin.—Colourless needles from benzene, m.p. 258–60°. Salkowski, Liebermann-Burchard and tetranitromethane reactions were negative. $[\alpha]_D^{28} = -23{\cdot}5° \pm 2°$ ($c = 1{\cdot}023$ in chloroform). Found: C, 84·7; H, 12·3. $C_{30}H_{50}O$ (friedelin) requires: C, 84·5; H, 11·8%.

The 2 : 4-dinitrophenylhydrazone[8] crystallized from chloroform-alcohol as shining orange-red plates, m.p. 301–05° (decomp.). Found: N, 9·7. $C_{36}H_{54}O_4N_4$ (friedelin 2 : 4-dinitrophenylhydrazone) requires: N, 9·2%.

The enol-benzoate, prepared as described by Corey and Ursprung[6] crystallized from ethyl acetate-chloroform as colourless plates, m.p. 262–65°,

$[\alpha]_D^{29} = +59{\cdot}3° \pm 2°$ ($c = 0{\cdot}922$ in chloroform). Found: C, 83·2; H, 10·7. $C_{37}H_{54}O_2$ (friedelin enol-benzoate) requires: C, 83·7; H, 10·3%.

Preparation of friedelan-3 α-ol[6].—A boiling solution of friedelin (0·3 g.) in *n*-amyl alcohol (30 ml.) was treated with sodium (0·6 g.) over a period of 15 minutes. Refluxing was continued until all the sodium had dissolved and the solvent was removed by distillation with steam. The resulting suspension was filtered, the precipitate washed, dried and crystallized from benzene-ethyl acetate, when colourless plates, m.p. 298–300°, were obtained. $[\alpha]_D^{28} = +17{\cdot}7° \pm 2°$ ($c = 1{\cdot}262$ in chloroform). Found: C, 84·7; H, 12·8. $C_{30}H_{52}O$ (epifriedelanol) requires: C, 84·1; H, 12·2%.

Epifriedelanol (*friedelan-3 β-ol*).—Colourless plates from chloroform, m.p. 280–82°. In the Salkowski reaction it gave a yellow colour gradually changing to orange-red. A red colour changing to deep pink was obtained in the Liebermann-Burchard reaction. No colour was obtained with tetranitromethane reagent. $[\alpha]_D^{28} = +25{\cdot}2° \pm 2°$ ($c = 0{\cdot}862$ in chloroform). Found: C, 84·5; H, 12·7. $C_{30}H_{52}O$ (epifriedelanol) requires: C, 84·1; H, 12·2%.

The acetate, prepared with pyridine and acetic anhydride, crystallized from benzene-acetone as colourless plates, m.p. 282–84°. $[\alpha]_D^{28} = +29{\cdot}3° \pm 3°$ ($c = 0{\cdot}724$ in chloroform). Found: C, 82·2; H, 11·8. $C_{32}H_{54}O_2$ (epifriedelanol acetate) requires: C, 81·6; H, 11·6%.

Preparation of friedelin from epifriedelanol[9].—Epifriedelanol (isolated from the leaves) was oxidised by reacting with chromic acid (just over one oxygen equivalent) in glacial acetic acid at 60–70° for half an hour. The product, on repeated crystallization from chloroform-benzene, yielded long colourless needles, m.p. 256–59°. $[\alpha]_D^{29} = -20{\cdot}8° \pm 2°$ ($c = 0{\cdot}983$ in chloroform). Found: C, 84·9; H, 11·9. $C_{30}H_{50}O$ (friedelin) requires: C, 84·5; H, 11·8%. The mixed m.p. with friedelin (isolated from the leaves) was undepressed.

Chloroform extract.—The extract was evaporated and the resulting dark-green semi-solid residue (*ca.* 150 g.) was extracted with hot acetone (750 ml.) when the wax and colouring matter went into solution. The insoluble material was filtered, washed, dissolved in excess of boiling alcohol (1·5 l.) (charcoal) and filtered. On leaving overnight the filtrate deposited a small quantity of wax which was filtered and rejected. The filtrate, on leaving aside for a number of days, slowly deposited a mass of colourless needles. The mother liquor, on further concentration, yielded two more crops of the same material (total yield: 18·1 g.). Crystallization from alcohol yielded

colourless needles, m.p. 282–83° (ursolic acid, 15·5 g.). $[\alpha]_D^{28} = +64{\cdot}7° \pm 2°$ ($c = 1{\cdot}12$ in absolute alcohol). Found: C, 78·7; H, 10·9. $C_{30}H_{48}O_3$ (ursolic acid) requires: C, 78·9; H, 10·6%. Colour in Liebermann-Burchard test: red-violet-blue-green. The acetate crystallized from alcohol as colourless needles, m.p. 281–82°. $[\alpha]_D^{28} = +68{\cdot}8° \pm 3°$ ($c = 0{\cdot}936$ in chloroform). Found: C, 76·7; H, 10·7. $C_{32}H_{50}O_4$ (ursolic acid acetate) requires: C, 77·1; H, 10·1%. Mixed melting points of the acid and its acetate with the respective authentic samples[2] were undepressed.

Alcohol extract.—The united dark red solution was concentrated under reduced pressure to 1 l. with occasional addition of water and left in the ice-chest for a few days, when a large amount of resin separated. The clear reddish-brown supernatant liquid was decanted, extracted with ether containing 3% alcohol (10 × 200 ml.) and the aqueous layer rejected. The united yellow ethereal extract was evaporated to a syrupy residue (5 g.) which was dried in a desiccator and treated with warm acetone (50 ml.), when most of it went into solution leaving behind a small quantity of yellow powder. Crystallization from absolute alcohol gave pale yellow needles (10 mg.). The substance did not melt below 350° and gave a negative reaction for anthoxanthins. It gave a yellow solution with aqueous sodium carbonate and a blue colour with alcoholic ferric chloride.

The residue obtained by evaporation of the acetone solution described above could not be crystallized. It was hydrolysed by boiling with 7% alcoholic sulphuric acid. The aglycone which was extracted with ether, on repeated crystallization from dilute alcohol and dilute acetone, yielded yellow needles, m.p. 304–07° (decomp.) (quercetin, 0·2 g.). It answered the colour reactions described for quercetin in the literature. Found: C, 59·9; H, 3·8. $C_{15}H_{10}O_7$ (quercetin) requires: C, 59·6; H, 3·3%. The acetate crystallized from alcohol as colourless needles, m.p. 196–98°. Found: C, 58·9; H, 4·3. $C_{25}H_{20}O_{12}$ (quercetin penta-acetate) requires: C, 58·6; H, 3·9%. Mixed m.p. with an authentic sample of penta-acetyl quercetin[1] was undepressed.

Summary

The examination of the leaves of *Rhododendron cinnamomeum* is described. The petroleum ether extract yielded epifriedelanol, friedelin and a minor component while the chloroform extract yielded ursolic acid. Quercetin and a minor component were obtained from the alcoholic extract.

Acknowledgments

We thank Dr. V. S. Rao, Conservator-General of Forests, West Bengal, and Mr. D. K. Dey, Divisional Forest Officer, Darjeeling Division, West

Bengal, for supplying the material used in this investigation along with its botanical identity. We thank Mr. R. V. Krishna Rao for the microanalyses.

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SEARCH FOR PHYSIOLOGICALLY ACTIVE COMPOUNDS

Part IV. Synthesis of 6- and 7-Halo Coumarins by Direct Condensation Procedures

By N. V. Subba Rao, F.A.Sc. and V. Sundaramurthy

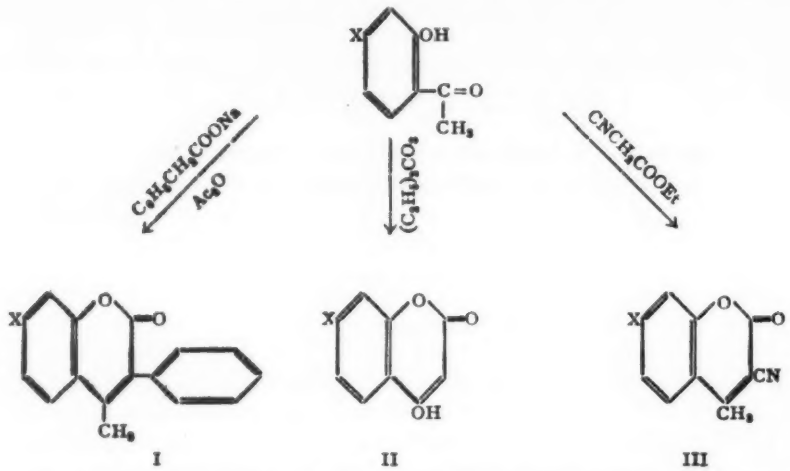
(Chemistry Department, Osmania University)

Received April 5, 1961

In earlier publications[1,2] from this laboratory the synthesis of 7-halo-4-methyl and 7-halo-4-methyl-3-phenyl coumarins by replacement of the amino group of the corresponding 7-amino coumarins adopting diazotisation followed by Sandmeyer reaction has been reported. These have now been synthesised by direct condensation procedures and have been shown to be identical with the compounds obtained by the diazo reaction. In addition, a number of 7-halo coumarins with different substituents in 3- and 4-positions have also been prepared by direct condensation for the study of their physiological properties.

Clayton[3] prepared 7-chloro and 7-chloro-4-methyl coumarins by the Pechmann condensation of *m*-chloro phenol. Buu-Hoi and co-workers[4] synthesised 7-bromo-3-aryl coumarins by the hydrolysis and cyclisation of the corresponding *β-o*-methoxyphenyl-*α*-phenylacrylonitriles using pyridine hydrochloride. In the present case, by the Pechmann condensation of *m*-bromo phenol, 7-bromo and 7-bromo-4-methyl coumarins have been prepared. 4-Halo-2-hydroxy acetophenones have been condensed with sodium phenylacetate and acetic anhydride adopting the procedure of Bargellini improved by Seshadri and co-workers,[5] with ethyl carbonate following Robertson's procedure[6] and with cyanoacetic ester adopting the procedure of Link and co-workers,[7] resulting in the formation of the corresponding 7-halo-4-methyl-3-phenyl (I) 7-halo-4-hydroxy (II) and 7-halo-4-methyl-3-cyano (III) coumarins respectively. The yields of 7-halo coumarins obtained by Pechmann condensation are comparatively poorer than those obtained by the diazotisation procedure, while the yields in the case of direct condensations making use of *o*-hydroxy acetophenones are comparatively better.

6-Bromo-4-methyl-3-phenyl coumarin has also been prepared by the condensation of 5-bromo-2-hydroxy acetophenone adopting Bargellini's procedure.



I II III

In tests using fish, the 7-bromo-4-methyl-3-phenyl coumarin is the most active among the compounds tested. The corresponding 6-bromo compound has less toxicity. The introduction of a hydroxyl in 4-position of 7-halo coumarins or a cyano group in 3-position of 7-halo-4-methyl coumarins does not seem to improve the toxicity but on the other hand appears to have a retarding effect.

Details of the fish toxicity data will be published elsewhere.

EXPERIMENTAL

1. *7-Bromo coumarin.*—*m*-Bromo phenol (5 g.), malic acid (5 g.) and concentrated sulphuric acid (13 ml.) were heated in an oil-bath at 120–30° C. till the evolution of carbon monoxide ceased. The reaction mixture was allowed to stand for two hours and then poured on crushed ice with stirring. The pasty mass that separated was repeatedly extracted with petroleum ether and the product obtained on removing the solvent was recrystallised from aqueous alcohol in colourless needles (0·15 g.), m.p. 105° C. (Found: C, 48·2; H, 2·3; Br, 35·2; $C_9H_5O_2Br$ requires C, 48·0; H, 2·2; Br, 35·5%).

2. *7-Bromo-4-methyl coumarin.*—*m*-Bromo phenol (5 g.) was condensed with ethyl acetoacetate (5 g.) in the presence of concentrated sulphuric acid (12 ml.). After 24 hours, the reaction mixture was poured on crushed ice and the solid that separated was filtered, washed free from acid and recrystallised from aqueous alcohol as colourless needles (0·5 g.), m.p. 138° C. Its mixed melting point with 7-bromo-4-methyl coumarin obtained earlier by the diazotisation procedure[2] was not depressed.

3. 7-*Chloro*-4-*methyl*-3-*phenyl coumarin*.—4-Chloro-2-hydroxy acetophenone[8] (4 ml.), sodium phenylacetate (8 g.) and acetic anhydride (50 ml.) were heated at 120° C. for half an hour and then at 180° C. for four hours in an oil-bath. The reaction mixture was then poured in cold water and allowed to stand overnight when a pasty mass separated. The water was decanted off and the pasty mass treated with cold alcohol. The solid obtained on filtration and recrystallisation from aqueous alcohol deposited colourless needles (4 g.), m.p. 140° C. Mixed melting point of the substance with the compound prepared earlier by the diazotisation procedure[1] was not depressed.

4. 7-*Bromo*-4-*methyl*-3-*phenyl coumarin*.—4-Bromo-2-hydroxy acetophenone was prepared adopting a procedure similar to the one in the preparation of 4-chloro-2-hydroxy acetophenone.[8] The bromo acetophenone (4 ml.) was condensed with sodium phenylacetate (8 g.) and acetic anhydride (50 ml.) as above and 7–bromo-4-methyl-3-phenyl coumarin (3 g.) was obtained as pale yellow needles from aqueous alcohol, m.p. 129° C. Its mixed melting point with the substance prepared earlier by diazotisation procedure[1] was not depressed.

5. 7-*Iodo*-4-*methyl*-3-*phenyl coumarin*.—4-Iodo-2-hydroxy acetophenone (0·1 g.) was condensed with sodium phenylacetate and acetic anhydride as in 3, and the product obtained (0·03 g.) on recrystallisation from aqueous alcohol gave greyish plates, m.p. 142° C. Its mixed melting point with the product obtained by diazotisation was not depressed.

6. 7-*Chloro*-4-*methyl*-3-*cyano coumarin*.—A mixture of 4-chloro-2-hydroxy acetophenone (2 ml.), ethyl cyanoacetate (2 g.) and sodium ethoxide (0·1 g. in 20 ml. absolute alcohol) was refluxed for about two hours when crystals began to appear. The mixture was cooled and the product separated was filtered. It was washed with small quantities of alcohol and recrystallised from acetone-water mixture as pale-yellow needles (1·4 g.), m.p. 204° C. (Found: C, 60·5; H, 3·2; Cl, 16·3; N, 5·9; $C_{11}H_6NO_2Cl$ requires C, 60·3; H, 3·4; Cl, 16·2; N, 6·3%).

7. 7-*Bromo*-4-*methyl*-3-*cyano coumarin*.—Starting from 4-bromo-2-hydroxy acetophenone (2 ml.) and adopting the procedure described above, 7-bromo-4-methyl-3-cyano coumarin was prepared as pale-yellow needles (1·2 g.), m.p. 210° C. (Found: C, 50·2; H, 2·8; N, 5·1; Br, 30·0; $C_{11}H_6NO_2Br$ requires C, 50·0; H, 2·3; N, 5·3; Br, 30·3%).

8. 7-*Chloro*-4-*hydroxy coumarin*.—4-Chloro-2-hydroxy acetophenone (1·5 ml.) was mixed with ethyl carbonate (10 ml.) in the presence of sodium

powder (1·5 g.) and after the initial vigorous reaction subsided, the reaction mixture was heated on a steam-bath for one hour. Alcohol was then added to destroy the excess of sodium and the excess ethyl carbonate removed by ether extraction. The product obtained was recrystallised once from ethyl alcohol and then from ethyl acetate-petroleum ether mixture as colourless needles (1 g.), m.p. 242° C. (Found: C, 54·8; H, 2·7; Cl, 18·0; $C_9H_5O_3Cl$ requires C, 55·1; H, 2·7; Cl, 18·1%).

9. *7-Bromo-4-hydroxy coumarin.*—Starting from 4-bromo-2-hydroxy acetophenone (1·5 ml.) and adopting the procedure described in 8, 7-bromo-4-hydroxy coumarin was prepared as colourless needles, m.p. 243° C. (Found: C, 44·0; H, 2·4; Br, 29·8; $C_9H_5O_3Br$ requires C, 44·5; H, 2·1; Br, 33·2%).

10. *6-Bromo-4-methyl-3-phenyl coumarin.*—5-bromo-2-hydroxy acetophenone[9] (2 g.), sodium phenylacetate (4 g.) and acetic anhydride (25 ml.) were condensed following the procedure described in 4. The product obtained was recrystallised from aqueous alcohol as light yellow needles (1·2 g.), m.p. 189° C. (Found: C, 61·4; H, 3·9; Br, 25·2; $C_{16}H_{11}O_2Br$ requires C, 61·0; H, 3·5; Br, 25·4%).

SUMMARY

7-Bromo and 7-bromo-4-methyl coumarins have been prepared by the Pechmann condensation of *m*-bromo phenol. From the halo-substituted *o*-hydroxy acetophenones, 7-halo-4-methyl-3-phenyl, 7-halo-4-hydroxy, 7-halo-4-methyl-3-cyano and 6-bromo-4-methyl-3-phenyl coumarins have been synthesised.

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TENSAMMETRIC STUDIES OF THIOUREA AND ITS DERIVATIVES*

By R. Narayan and V. K. Venkatesan

(*Central Electrochemical Research Institute, Karaikudi-3*)

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(Communicated by Professor K. S. G. Doss, F.A.SC.)

Abstract

Adsorption of thiourea and some of its derivatives at the mercury-solution interface has been studied by the tensammetric technique. It has been found that adsorption of thiourea increased the differential capacity rather than decreasing it. However the adsorption of S-methyl derivative of thiourea decreased the differential capacity. The N-substituted derivatives depressed the tensammetric curve of the supporting electrolyte to a greater extent than the N, N¹-substituted derivatives. The different behaviours of thiourea and its derivatives are discussed.

Edsberg,[1] Jensowsky,[2] Zuman *et al.*[3] made a systematic study of thiourea and its derivatives by D.C. polarographic method. They have arrived at the conclusion that thiourea is adsorbed at the mercury surface, which gives rise to an adsorption wave. Schapink *et al.*[4] have also deduced from the results of differential capacity and interfacial tension measurements, that thiourea is adsorbed at the mercury surface.

Normally the adsorption of surface-active substances at the interface results in a lowering of the differential capacity. Schapink *et al.*, however, find that the differential capacity values are greater in the presence of thiourea than in 0·1 M. sodium fluoride alone.

With a view to elucidate the phenomenon, tensammetric studies of thiourea and some of its derivatives are made in 0·1 M. perchloric acid, 0·1 M. sodium perchlorate and 0·1 M. KCl.

Experimental

Perchloric acid, sodium perchlorate and potassium chloride are of Merck G.R. quality. Thiourea of purest variety is used in all the investigations. S-methyl derivative of thiourea is prepared following the method

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given in organic syntheses by Blatt.[5] The recrystallised product is used in the above studies. The mono and disubstituted derivatives of thiourea have been kindly spared by Dr. J. J. Trivedi of University College of Science, Ahmedabad. The experimental set-up is the same as that used by Doss and co-workers.[6] Other characteristics of the dropping mercury electrode are as follows:

h	..	58 cm.
t	..	5·8 sec. in 0·1 M. KCl (open circuit)
m	..	0·90 mg.sec.$^{-1}$
A.C. ripple		30 mv. (r.m.s.)
D.C. Voltages are all with respect to saturated calomel electrode (SCE).		

Except when stated otherwise, the solutions are not deaerated.

RESULTS AND DISCUSSION

Figures 1 and 2 show the tensammetric curves of thiourea and S-methyl isothiouronium sulphate in 0·1 M. perchloric acid and 0·1 M. sodium perchlorate. The results of other mono and disubstituted derivatives of thiourea are represented in Fig. 3.

The tensammetric curves of those substances which can be adsorbed are normally below that of the indifferent electrolyte up to their desorption potentials. It will be observed from Figs. 1 and 2 that the tensammetric curves of thiourea are above that of 0·1M. perchloric acid and 0·1M. sodium perchlorate at all potentials. From the above one is apt to conclude that thiourea is not adsorbed at the mercury surface. However, the interfacial tension measurements of Schapink *et al.* showed that thiourea is adsorbed. The drop time *vs.* potential studies made by us also show that thiourea is adsorbed at the positive side of the electrocapillary zero. Thus, it is seen that though there is adsorption, the tensammetric curves (the differential capacity curves) of thiourea are above that of the supporting electrolyte. This may probably be explained in the following manner. Since the thiourea molecule is specifically adsorbed (chemisorption), the effective thickness* of the double layer might be less than that in the absence of thiourea molecule and the differential capacity may get increased. The steep rise observed in Fig. 1 at potentials more positive than $-0{\cdot}10$ V. is either due to electro-

* The increase in the capacity may be due to a change in dielectric constant and/or thickness of the double layer. The combined effect is taken into account in terms of effective thickness.

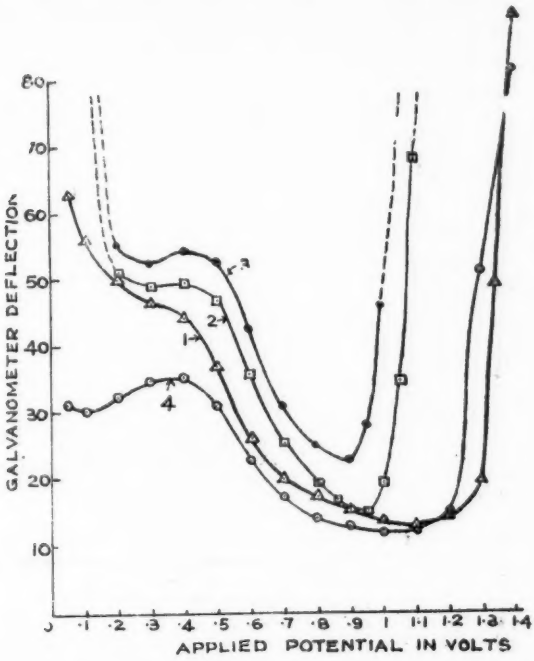


FIG. 1. Tensammetric curves of thiourea and S-methyl isothiouronium sulphate in 0·1 M. perchloric acid.

Curve 1. Supporting electrolyte.
Curve 2. 0·05% thiourea.
Curve 3. 0·1% thiourea.
Curve 4. 0·1% S-methyl derivative.

strictional effects[7] or due to anodic reaction of mercury with the thiourea molecule. However, the sharp rise observed at voltages more negative than $-1{\cdot}0$ V. is due to hydrogen discharge. Thiourea brings down the hydrogen over-voltage and hence the hydrogen discharge takes place at a potential more positive by about 0·2 V. than in the absence of thiourea.

The S-methyl derivative exhibits the normal behaviour of a surfactant, *i.e.*, the tensammetric curves are below that of the supporting electrolyte which can be seen from Figs. 1 and 2. This is probably due to the fact that the presence of $-CH_3$ group prevents the sulphur atom from coming very close to the mercury surface thereby increasing the effective thickness of the double layer. It is to be pointed out however that the depression of capacity due to adsorption is on the lower side for a substance which may

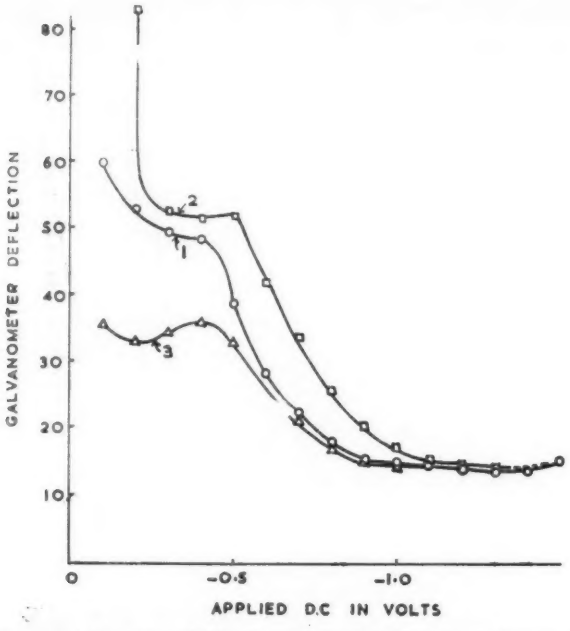
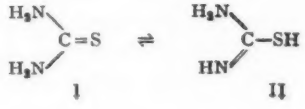


FIG. 2. Tensammetric curves of thiourea and S-methyl isothiouronium sulphate in 0·1 M. sodium perchlorate.

Curve 1. Supporting electrolyte.
Curve 2. 0·1% thiourea.
Curve 3. 0·1% S-methyl derivative.

be expected to be strongly adsorbed. This may be due to the effective thickness of the double layer not being much higher than that in the case of the supporting electrolyte. Similar explanation may be given to the observations made in this laboratory earlier with thiourea in 1 M. H_2SO_4 solution.[8] The steep rise observed with thiourea at potentials more positive than $-0{\cdot}1$V. is not exhibited by the S-methyl derivative either in acid solution or sodium perchlorate solution. The substitution of H by $-CH_3$ group probably prevents the electrostrictional and/or anodic oxidation effects.

The prevention of anodic oxidation can be understood from the following mechanism. Thiourea can have the following two tautomeric forms:



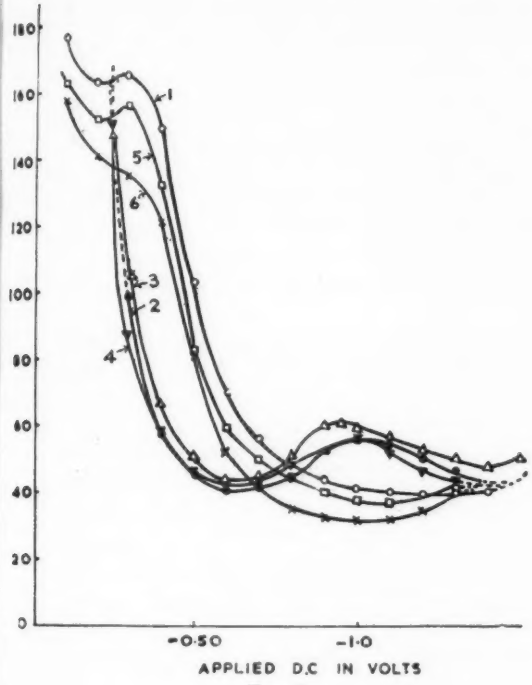


FIG. 3

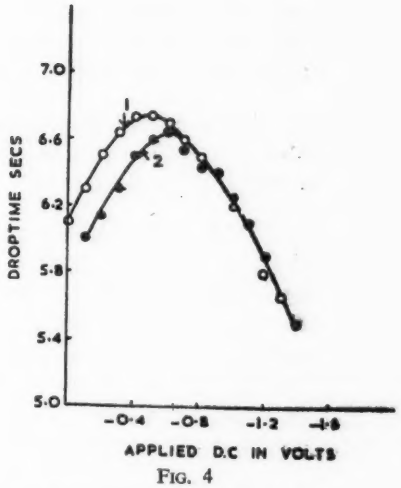


FIG. 4

FIG. 3. Tensammetric curves of N-substituted derivatives of thiourea in 0·1 M. KCl.

Curve 1. Supporting electrolyte.
Curve 2. Saturated solution of *o*-bromo-benzyl thiourea.
Curve 3. Saturated solution of *m*-bromo-benzyl thiourea.
Curve 4. Saturated solution of *p*-bromo-benzyl thiourea.
Curve 5. Saturated solution of *o*-bromobenzyl-benzyl thiourea.
Curve 6. Saturated solution of *o*-chlorobenzyl-benzyl thiourea.

FIG. 4. Drop time—Potential curves in 0·1 M. sodium perchlorate.

Curve 1. Supporting electrolyte.
Curve 2. 0·1% thiourea.

The —SH group in the second form is easily oxidised. The substitution of the H in the SH group by CH_3 group does not permit the intramolecular rearrangement which can give the —SH group.

The tensammetric curves of five N-substituted thiourea derivatives, both mono and disubstituted, are depicted in Fig. 3. All the curves are below that of 0·1 M. KCl, which is the indifferent electrolyte. At the positive side of the electrocapillary zero, the curves of mono-substituted derivatives,

m-, and *p*-chloro-benzyl thioureas are well below that of 0·1 M. KCl and show as high as 60% depression. The disubstituted derivatives (*viz.*, *o*-chlorobenzyl-benzyl thiourea and *o*-bromobenzyl-benzyl thiourea) however show relatively a small depression. Due to the presence of bulky hydrophobic groups these disubstituted derivatives can be expected to be more strongly adsorbed than the mono-derivatives. It is possible, however, that the substituents do not lie on the same plane so that the steric effect may hinder the adsorption to some extent, and the molecule may be adsorbed with the sulphur atom close to the mercury. This may decrease the effective thickness of the double layer and increase the differential capacity.

In the case of mono-substituted derivatives a small hump is noted round about −1·0 V. This may be due to the desorption of the derivatives over a range of potentials.

Further the tensammetric curves of the mono-substituted derivatives show a sharp rise from −0·25 to zero volt, similar to thiourea. This again may be due to the anodic reaction and/or electrostriction effects. However, this behaviour is not exhibited up to about −0·10 V. by the di-substituted derivatives. The substitution of one hydrogen atom in both the NH_2 groups by phenyl or benzyl groups shifts the $E_{\frac{1}{4}}$ of the anodic waves of these derivatives, to more positive potentials. Hence the steep rise is not observed in the case of N, N^1-substituted derivatives even up to 0 V.

It appears that the position of the halogen atoms in the benzene nucleus of the substituents does not affect much the behaviour of the derivatives.

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ON THE EXISTENCE AND UNIQUENESS OF FLOWS BEHIND THREE-DIMENSIONAL CURVED STOCKS

By J. N. Kapur

(Indian Institute of Technology, Kanpur)

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Introduction

By using Cauchy-Kowaleski theory, Taub[1] discussed the existence and uniqueness of flows behind two-dimensional stationary and pseudo-stationary curved shocks. Later Kanwal[2] generalised his results for flows behind three-dimensional stationary and pseudo-stationary shocks. In their treatment, the existence theorem is applied after reducing the basic equations of gas dynamics to the 'normal' form by using the formal methods of tensor analysis. It is shown in the present paper that it is simpler to apply Cauchy-Kowaleski theory directly to the equations without first transforming them. The same method is used for discussing the conditions for the existence and uniqueness of flows behind unsteady curved shocks as well as flows behind curved shocks in three-dimensional magnetogas-dynamics.

The Basic Equations and Shocks Conditions

The shock surface divides the flow into two regions 1 (in front of the shock) and 2 (behind the shock). For the case of an ideal stationary gas with viscosity and heat conductivity zero, the following equations hold on both sides of the shock surface:

$$\rho, iu_i + \rho u_j, j = 0 \quad \text{(equation of continuity)} \tag{1}$$

$$p, i + \rho u_j u_i, j = 0 \quad \text{(equation of motion)} \tag{2}$$

$$u_i S, i = 0 \quad \text{(equation of energy)} \tag{3}$$

$$p - \rho^{\gamma} . e^{S/JC_v} = 0 \quad \text{(equation of state)} \tag{4}$$

where p, ρ, S and u_i denote the pressure, density, entropy and velocity components respectively. From (3) and (4) we get on eliminating S,

$$u_i, j u_i u_j - c^2 u_k, k = 0, \quad c^2 = \frac{\gamma p}{\rho} . \tag{5}$$

Let u_{1i}, p_1, ρ_1 and u_{2i}, p_2, ρ_2 denote the values of the variables immediately in front of and behind the shock surface, then the Rankine-Hugoniot conditions for the stationary shock are:

$$u_{2i} - u_{1i} = -\frac{\delta}{1+\delta} u_{1n} n_i; \quad p_2 - p_1 = \frac{\delta \rho_1 u_{1n}^2}{1+\delta}, \quad \rho_2 - \rho_1 = \delta \rho_1, \tag{6}$$

where n_i are the components of the normal to the shock surface directed from region 1 into region 2, and

$$u_{1n} = u_{1i} n_i, \quad u_{2n} = u_{2i} n_i \tag{7}$$

$$\delta = \frac{2(\rho_1 u_{1n}^2 - \gamma p_1)}{2\gamma p_1 + (\gamma - 1)\rho_1 u_{1n}^2}. \tag{8}$$

Existence and Uniqueness of Flows behind Three-Dimensional Stationary Curved Shocks

Omitting the suffix 2 for the quantities behind the shock, the five partial differential equations of the first order for the five variables u_1, u_2, u_3; p, ρ are given by (1), (2) and (5). Knowing the flow in front of the shock and the equation of the shock surface, equations (6) determine the values of these variables on the shock surface for the flow in region 2. The Cauchy-Kowaleski condition for the existence of the flow behind the shock is:

$$\begin{vmatrix} \rho n_1 & \rho n_2 & \rho n_3 & 0 & u_1 n_1 + u_2 n_2 + u_3 n_3 \\ \rho(u_1 n_1 + u_2 n_2 + u_3 n_3) & 0 & 0 & n_1 & 0 \\ 0 & \rho(u_1 n_1 + u_2 n_2 + u_3 n_3) & 0 & n_2 & 0 \\ 0 & 0 & \rho(u_1 n_1 + u_2 n_2 + u_3 n_3) & n_3 & 0 \\ (u_1^2 - c^2) n_1 + u_1 u_2 n_2 + u_1 u_3 n_3 & u_2 u_1 n_1 + (u_2^2 - c^2) n_2 + u_2 u_3 n_3 & u_3 u_1 n_1 + u_3 u_2 n_2 + (u_3^2 - c^2) n_3 & 0 & 0 \end{vmatrix} \neq 0 \tag{9}$$

or

$$\rho u_n^4 \left(1 - \frac{c^2}{u_n^2}\right) \neq 0, \tag{10}$$

but

$$1 - \frac{c^2}{u_n^2} = -\frac{\gamma + 1}{2} \delta.$$

Since $\delta > 0$ for a shock of non-zero strength, the required condition is

satisfied and there exists a unique analytic flow behind a steady curved shock. We may note that (9) is the same condition as obtained in [1] and [2].

EXISTENCE AND UNIQUENESS OF FLOWS BEHIND THREE-DIMENSIONAL NON-STATIONARY CURVED SHOCKS

The basic equations in this case are:

$$\rho, t + u_j \rho, j + \rho u_j, j = 0 \tag{11}$$

$$\rho u_i, t + p, i + \rho u_j u_i, j = 0 \tag{12}$$

$$S, t + u_i S, i = 0 \tag{13}$$

From (4) and (13)

$$p, t + u_j p, j = c^2 (\rho, t + u_j \rho, j) \tag{14}$$

Using (11), (12) and (14)

$$-\rho^{-1} p, t + u_i u_i, t + u_i u_j u_i, j - c^2 u_j, j = 0. \tag{15}$$

Equations (11), (12) and (15) constitute the five partial differential equations of the first order for determining the five functions u_1, u_2, u_3, p, ρ of the four independent variables x_1, x_2, x_3, t.

Let the equation of the shock surface be

$$s(x_1, x_2, x_3, t) = 0. \tag{16}$$

For the flow behind to exist and be unique, the determinant $\triangle$ should not vanish, where

$$\triangle \equiv \begin{vmatrix} \rho s_{,1} & \rho s_{,2} & \rho s_{,3} & 0 & u_1 s_{,1} + u_2 s_{,2} + u_3 s_{,3} + s, t \\ \rho [u_1 s_{,1} + u_2 s_{,2} + u_3 s_{,3} + s, t] & 0 & 0 & s_{,1} & 0 \\ 0 & \rho [u_1 s_{,1} + u_2 s_{,2} + u_3 s_{,3} + s, t) & 0 & s_{,2} & 0 \\ 0 & 0 & \rho [u_1 s_{,1} + u_2 s_{,2} + u_3 s_{,3} + s, t] & s_{,3} & 0 \\ (u_1^2 - c^2) s_{,1} + u_1 u_2 s_{,2} + u_1 u_3 s_{,3} + u_1 s, t & u_2 u_1 s_{,1} + (u_2^2 - c^2) s_{,2} + u_2 u_3 s_{,3} + u_2 s, t & u_3 u_1 s_{,1} + u_3 u_2 s_{,2} + (u_3^2 - c^2) s_{,3} + s, t & -\frac{1}{\rho} s, t & 0 \end{vmatrix} \tag{17}$$

Let

$$n_i = \frac{s,\, t}{\sqrt{s^2{}_{,1} + s^2{}_{,2} + s^2{}_{,3}}} \ (i = 1, 2, 3), \quad n_4 = \frac{s,\, t}{\sqrt{s^2{}_{,1} + s^2{}_{,2} + s^2{}_{,3}}} \tag{18}$$

and

$$u_n = u_1 n_1 + u_2 n_2 + u_3 n_3, \tag{19}$$

then the condition becomes on simplification

$$(u_n + n_4)^3 \{(u_n + n_4)^2 - c^2\} \neq 0. \tag{20}$$

Now at the shock surface if v_1, v_2, v_3 are the velocity components for the shock, then

$$s,_1 v_1 + s,_2 v_2 + s,_3 v_3 + s,_t = 0$$

or

$$n_1 v_1 + n_2 v_2 + n_3 v_3 + n_4 = 0, \tag{21}$$

so that

$$\begin{aligned} u_n + n_4 &= u_n - n_i v_i = n_i u_i - n_i v_i \\ &= n_i (u_i - v_i) = n_i \mathrm{U}_i = \mathrm{U}_n \qquad \text{(say)}. \end{aligned} \tag{22}$$

Thus the condition is given by

$$1 - \frac{c^2}{\mathrm{U}_n{}^2} = -\frac{\gamma + 1}{2}\,\delta \neq 0 \tag{23}$$

which is satisfied in the case of a shock of non-zero strength. The present result generalises the results of [1] and [2] for pseudo-stationary shocks and shows that even in the most general case, the result obtained there holds.

Condition for the Existence of Flows behind Three-Dimensional Curved Shocks in Magneto-Gasdynamics

Assuming zero viscosity, zero heat conductivity and infinite electrical conductivity, the basic equations of magneto-gasdynamics to be satisfied on both sides of the shock are[4]:

$$u_j \mathrm{H}_{i,\,j} - \mathrm{H}_j u_{i,\,j} + \mathrm{H}_i u_{j,\,j} = 0 \tag{24}$$

$$u_j u_{i,\,j} - \frac{\mu e}{\rho}\,\mathrm{H}_j \mathrm{H}_{i,\,j} + \frac{1}{\rho}(p,\, i + \mu_e \mathrm{H}_j \mathrm{H}_{j,\,i}) = 0 \tag{25}$$

$$u_j \rho,\, j + \rho u_{j,\,j} = 0 \tag{26}$$

$$u_j p,\, j - c^2 u_j \rho,\, j = 0. \tag{27}$$

(17)

These are eight partial differential equations for the eight variables u_1, u_2, u_3, H_1, H_2, H_3, p, ρ. The values of these immediately in front are to be determined by generalised Rankine-Hugoniot relations. From Cauchy-Kowaleski theory the flow will exist behind the shock if the following eighth order determinant Δ' does not vanish.

$$\Delta' = \begin{vmatrix} -H_n + H_1 n_1 & H_1 n_2 & H_1 n_3 & u_n & 0 & 0 & 0 & 0 \\ H_2 n_1 & -H_n + H_2 n_2 & H_2 n_3 & 0 & u_n & 0 & 0 & 0 \\ H_3 n_1 & H_3 n_2 & -H_n + H_3 n_3 & 0 & 0 & u_n & 0 & 0 \\ \frac{\rho}{\mu_e} H_n & 0 & 0 & H_1 n_1 - H_n & H_2 n_1 & H_3 n_1 & \frac{1}{\mu_e} n_1 & 0 \\ 0 & \frac{\rho}{\mu_e} u_n & 0 & H_1 n_2 & H_2 n_2 - H_n & H_3 n_2 & \frac{1}{\mu_e} n_2 & 0 \\ 0 & 0 & \frac{\rho}{\mu_e} u_n & H_1 n_3 & H_2 n_3 & H_3 n_3 - H_n & \frac{1}{\mu_e} n_3 & 0 \\ n_1 & n_2 & n_3 & 0 & 0 & 0 & 0 & \frac{u_n}{\rho} \\ 0 & 0 & 0 & 0 & 0 & 0 & -u_n & c^2 u_n \end{vmatrix} \neq 0 \quad (28)$$

where H_n and u_n are the normal components of the magnetic and velocity fields immediately behind the shock. For two-dimensional flows, this reduces to a sixth order determinant. Its particular cases as well as the corresponding condition for non-steady case will be discussed separately. The aim above is to show that the direct method is very simple to apply even in the more general case of magneto-gasdynamics. It need hardly be pointed out that the method of Taub and Kanwal is not at all applicable in this case.

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